IV. ENVIRONMENTAL DATA

Sampling Methods

In atmospheric sampling for airborne HF, the usual gaseous sampling considerations (ie, flowrate, fluid volume, pressure, and temperature) are occasionally complicated by the presence of particulate forms of fluoride or dust particles which can adsorb gaseous HF. [61-66]

The recommended sampling method should allow for the collection of total fluorides as well as for the separation of gaseous HF from particulates for the purpose of determining the ceiling concentrations of HF. The method of separation should include a means of releasing adsorbed HF from particulate matter and combining it with the existing gaseous sample. The National Academy of Sciences [67] has summarized much of the data available on air sampling and treatment of biologic samples.

Sampling methods that separate gaseous from particulate fluoride rely on the reactivity of the gaseous forms with aluminum, alkaline, or other materials. Habel [64] used a quartz filter device containing a membrane filter followed by a series of impingers to achieve a separation of the gaseous and particulate fluoride components. He found that as relative humidity of air increased, the amount of HF sorbed on the membrane filter increased. When the quartz filter holder was heated during sampling, loss due to sorption of HF on filters was markedly reduced. Heating the filter holder aided in the transfer of sorbed HF from the filter to the impingers. Pack et al [68] used an assembly of three concentric aluminum tubes attached to an impinger to accomplish a sharp separation of gaseous and particulate compounds. A less distinct separation occurred when sodium

bicarbonate-coated glass tubes were used in conjunction with an impinger. Mandl et al [62] found that when sodium bicarbonate-coated glass tubes were used, efficiency of gaseous uptake was affected by tube diameter. They [62] also used a tape sampler composed of two treated tapes, one to remove particulates and one to remove gaseous fluoride compounds.

Several investigators reported that impregnation of filters with potassium carbonate [69] and lime [70-73] allowed collection of hydrogen fluoride, but no efficiencies for separation of particulate and gaseous components were noted. Glass-fiber filters were evaluated by Pack and Hill [74] and Pack et al. [75] The glass-fiber filter was found to be a simple, rugged system for efficient collection of both gaseous and particulate fluorides, but suffered from high blank values.

Pack et al [68] found that standard impingers were very satisfactory for collecting gaseous and particulate fluorides. Bourbon [76] tested the HF collection efficiencies of four impingers in series in an industrial atmosphere. He found that for test durations of less than 12 hours, all of the HF was recovered by the first impinger. Mandl et al [62] compared hydrogen fluoride collection efficiencies of a paper-tape sampler and impingers and found essentially no difference in efficiency.

Panin [63] developed a method for the separate determination of inorganic aerosols of water-soluble fluorine compounds and gaseous compounds in the atmosphere using a titanium-chromotropic reagent. The aerosols were sorbed by a cellulose acetate filter and the gases (unspecified) in an absorbent solution. Separation efficiencies were not noted. Elfers and Decker [61] drew 28 μg of fluoride (HF gas) through two membrane filters impregnated with sodium formate. The amount of HF

collected on the first filter was "statistically equivalent" to the amount introduced. The study was repeated using unimpregnated filters. The first filter retained approximately 30% of the fluoride introduced. Bourbon [76] used impingers containing 0.1 N sodium hydroxide and untreated 0.8-μm membrane filters and determined the filters were more efficient for recovery of HF than the impingers, but were occasionally prone to clogging during dusty, humid conditions. Mandl et al [62] tested many materials for their capacity to remove particulate fluoride without affecting passage of hydrogen fluoride, and determined that citric acid-treated 1-μm pore filter paper was approximately 99% efficient in allowing the passage of hydrogen fluoride. They found untreated filters could retain up to 50% of the hydrogen fluoride. A separation efficiency comparison was then made between a dual filter sampler (citric acid-treated prefilter and a secondary filter impregnated with sodium hydroxide and glycerol) and a citric acid-treated prefilter preceding or following a bicarbonate-coated tube system. The systems were comparable in separation efficiency, but the coated tube system was adversely affected by humidity. Dorsey and Kemnitz [65] brought about the separation by using a heated glass probe for converting hydrogen fluoride to silicon tetrafluoride before filtration and various combinations of treated prefilters and impingers. The sampling train was complex and required a probe temperature of 182 C. Pack et al [75] found that, depending on the degree of dust loading, the amount of hydrogen fluoride retained on an untreated membrane filter varied from 17-83%.

Jahr [66] effected the separation of gaseous HF from particulate materials by drawing air through an untreated primary membrane filter

followed by a sodium formate-treated secondary filter. The filters were held in a small plastic personal sample cassette (field monitor) which was warmed for 4 hours at 75 C after sampling to drive adsorbed HF from the primary to the secondary filter. [66] A comparison of the separation of particulate materials and HF by dual membrane filtration with and without postsample filter heating showed a gaseous to particulate ratio of 20.5:70.5 without heating and 80:20 with heating. He determined that better than 99% recovery could be accomplished within 4 hours by heating the filters to 75 C.

While the sampling method developed by Jahr [66] appears to have merit, further evaluation is necessary before it can be considered a recommended NIOSH procedure. It must be determined whether the capacity of both the treated and the untreated filters is great enough to efficiently retain the amounts normally sampled in the workplace. Fluoride filter blank values must be known so that sampling rates and sample durations can be realistically determined.

The method recommended for sampling for airborne hydrogen fluoride utilizes a midget bubbler and a fluoride ion-selective electrode. [77] A known volume of air is drawn through a midget bubbler, placed in the breathing zone of the worker, containing sodium hydroxide to trap the hydrogen fluoride. The resulting solution is diluted with total ionic strength activity buffer (TISAB) and then analyzed using a fluoride ion-selective electrode.

This method is simple and allows for quick analysis. The "personal sampler" approach permits realistic short-term or extended period monitoring of on-the-site worker exposures and allows for the computation

of time-weighted average exposures.

Unlike the previously mentioned method, [66] the range and sensitivity of the bubbler method, as well as the collection efficiency, have been determined. The entire method has also been extensively field-tested. [77]

The bubbler method does not provide for the separation of gaseous and particulate fluorides which is necessary when samples are taken to determine ceiling concentrations. It may be possible when sampling to determine a ceiling to use an assembly consisting of an untreated membrane filter followed by a bubbler to effect the separation of gaseous and particulate fluorides. The membrane filter would retain particulate matter and allow passage of HF into the bubbler where it could be collected and analyzed following the recommended procedure for analysis. It is possible that significant amounts of HF might be absorbed by particulate matter retained on the primary filter, thus interfering with total passage of HF to the impinger. This problem has been effectively controlled in analagous sampling situations. Jahr [66] found that adsorbed HF was transferred from an untreated primary filter to a secondary filter when it was heated. Habel [64] tested a sampling assembly consisting of a membrane filter followed by an impinger. He found that heating the filter holder markedly reduced the amount of adsorbed HF retained by the filter and filter holder.

The above studies [64,66] indicate that separation of gaseous and particulate fluorides may be accomplished by the use a filter-bubbler sampling assembly. Extensive testing is necessary, however, before this method or a similar method can be recommended.

Analytical Methods

Many manual and semiautomatic methods for analysis of hydrogen fluoride as fluoride are available. The selection of a method depends upon the type of sampling, separation, sensitivity, and accuracy required. Titrimetric methods were among the first to be used effectively for analyzing the HF collected in air samples. [78] A frequently used complexing agent is thorium with alizarin red as the end-point dye. [79,80] Many modifications of this general technique have been made using various dyes and complexing agents. [78,81-83] Nielsen and Dangerfield [84] used an anion exchange resin to form hydrofluoric acid which was titrated with base. A detailed discussion of most of the methods for HF analysis known through 1950 is contained in reviews by McKenna. [85-87] The Intersociety Committee [88] has published tentative methods of analysis based on techniques developed prior to 1970.

Trace amounts of fluoride ion may be estimated directly in body fluids or water by measuring their inhibitory effect on the enzymatic hydrolysis of ethyl butyrate. [89] The first successful colorimetric analytical method in which thorium with an alizarin sulfonate lake was decolorized (bleached) by fluoride was presented in 1943. [80] Modifications to the method were reported in 1951 [90] and 1955. [91] Another colorimetric method involved the use of zirconium-alizarin sulfonate. [92] A bleaching system developed by Megregian [93] in 1953 used zirconium-eriochrome cyanine-R complex. This method was used by many laboratories [88,94-97] because it was considered to be very accurate, and establishment of the reaction equilibrium occurred rapidly. [28,93] In 1954, Belcher [98] introduced alizarin complexone which formed a red

chelate with cerium-III and formed a stable blue complex in the presence of fluoride ions. A colored complex of lanthanum(III)-alizarin complexone was also used. [99-101] Other dyes which have been suggested are thorium-chrome azurol-S, [102] aluminum-dyes, [103] and iron(III) complexes. [104] In 1958, Bellack and Schouboe [105] introduced trisodium 4,5-dihydroxy 3-(p-sulfophenylazo) 2,7-naphthalene disulfonate (SPADNS) as a dye for use with zirconium. It proved more stable and provided more rapid analysis than zirconium-alizarin photometric methods, and had a broader absorption spectrum, making it easier to use with simple filter photometers. This system could be substituted in many procedures based on the zirconium-alizarin system. [106,107] The zirconium-xylenol orange method was devised after the zirconium-SPADNS method. A positive color was formed through a catalytic action which had greater sensitivity than the older bleaching methods. [108] Other metal-dye complex systems have been used, although not widely applied. [63,109] Noteworthy among them is the fluorescence quenching technique using magnesium 8-hydroxyquinoline. [110]

In summary, the colorimetric methods frequently cited in the literature are zirconium-alizarin, zirconium-SPADNS, zirconium-eriochrome cyanine-R complex, and lanthanum(III)- or cerium(III)-alizarin complexone systems. Differences were found in sensitivity and some interfering agents, eg, chloride, caused bleaching similar to that caused by fluoride.

Polarographic and other electrochemical methods [111] have been developed for fluoride but have not been widely accepted.

Recent development of gas chromatographic detection methods for fluoride [112-116] aids in the detection of gaseous fluorides in the presence of particulate fluorides by allowing analysis of gaseous

components while excluding particulate components. X-ray diffraction was applied to fluoride analysis by Lennox and Leroux. [117] Neutron activation analysis was applied by Spoonemore [118]; atomic absorption spectrometry, [119] nondispersive infrared analysis, [120] and pyrohydrolysis [121] have also been used for analyzing fluoride. Mass spectrometric methods [122] have not been widely used. With the exception of the colorimetric methods, the previously mentioned instrumental methods have not gained wide acceptance.

A number of fully automatic and semiautomatic sampling instruments have been devised for the measurement of fluoride levels in air and urine. [94,99,110,123-134] Most of these methods involve rather elaborate colorimetric procedures which are not generally suitable to the practical industrial hygiene laboratory or as an in-plant monitor.

The development of the fluoride ion-selective electrode provided a rapid, direct method of analysis with only minimal interferences. [135] The electrode employs a crystal that develops a potential dependent primarily on fluoride ion activity which is measured relative to a reference electrode by a millivolt meter. Methods have been published for analysis of fluoride in air and stack samples, [61] blood and plasma, [136] urine, [136-141] bones, [132] teeth, [142] and other materials. [121,132,136] A comparison was made between SPADNS and electrode methods for stack emission samples. [143] No difference in analytical results was noted.

The fluoride ion-selective electrode has made routine measurement of urinary fluoride concentrations easy and rapid. [138,139,144] It offers a rapid, simple, and most selective method for determining fluorides in urine

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when used between pH values of 4.5-8. [135,138]

Although in some cases interfering substances make prior preparation or separation of the sample necessary before the final analysis with the electrode, [132,135] the great working range of concentration makes the electrode method very useful (0.03 μg/ml to 20 mg/ml with sufficient precision ($\pm$1%) for most determinations. [61,112,132,145-147]

The method outlined by the American Society for Testing and Materials [148] is commonly applied, with minor modifications, to collected air samples of soluble fluorides and to urine samples.

The sampling and analytical procedures recommended by NIOSH for hydrogen fluoride in an air sample involves adding 0.1 N sodium hydroxide to the contents of a bubbler after sampling has been conducted and then further diluting the sample with TISAB; if a urine sample is involved, equal volumes of urine and TISAB are mixed. [138] Subsequently, in either case, direct measurement with a fluoride ion-selective electrode is then made. The relative adaptability, ease of analysis, reproducibility, and linearity of response over an analytical range of nearly 100,000 provide a sound basis for using the electrode. Any alternative method should provide the recommended allowable air concentration (2.5 mg F/cu m air) as an intermediate level of reliable detectability. For example, if the F concentration in the air sampled is 2.5 mg/cu m, a 10-minute sample collected at 1.0 liter/minute will contain 0.025 mg F which corresponds to 0.6 ppm in the analytical solution (see Appendix II). This quantity is about 20 times that necessary for analysis (0.02-0.03 ppm). [79,132]

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Environmental Levels and Engineering Controls

A search of the literature for environmental studies of hydrogen fluoride exposure revealed a significant gap. Only two studies [46,49] were located which reported workroom exposure levels in the manufacturing of hydrogen fluoride, and none was found describing workroom exposure levels in industrial processes using the major portion of the hydrogen fluoride produced in this country, namely, the manufacture of fluorocarbon compounds, the manufacture of synthetic cryolite and aluminum fluoride, and the use of hydrogen fluoride as a catalyst in alkylation processes. [17] It may be that these processes are completely enclosed and therefore do not produce any workroom environmental exposure, but this has not yet been confirmed. The majority of the studies found were concerned with the generation of hydrogen fluoride incidental to other processes.

Engineering controls were often mentioned or recommended, but few details of control installations were reported, and in most cases effectiveness of controls was not determined by actual measurement. Generally, except for emergencies, hydrogen fluoride levels in the processes reported were not grossly excessive, suggesting that effective control was readily obtainable by standard methods. The following studies, categorized by type of industrial operation, have been selected as examples.

(a)   Manufacture of Hydrogen Fluoride

In 1940, Machle and Evans [46] published a study of workmen exposed principally to hydrogen fluoride during the manufacture of hydrofluoric acid. The plant started production in 1931, at which time clinical studies were begun. The authors mentioned that most of the men had received

treatment for skin burns, but had exhibited no general signs or symptoms of injury from fluorine, presumably in the form of hydrogen fluoride or fluorides. According to the authors, mechanical difficulties and operational changes initially led to frequent "fairly severe" exposures. At the time of reporting, they stated that ventilation facilities ordinarily kept the atmosphere free of HF acid "fumes," and that the "fluorine" exposure had been reduced to the lowest practical level. Unanticipated leaks and repair operations were responsible for occasional higher exposures. No "fluorine" (presumably fluoride) was detected in the center of the building under normal operating conditions, while three samples taken near equipment or during repairs revealed 0.011-0.021 mg fluorine/liter (11-21 mg F/cu m). Machle and Evans [46] concluded that the exposure was excessive, although it was intermittent.

In 1967, the US Public Health Service reported [49] an environmental health survey of a chemical plant producing primarily sulfuric, phosphoric, and hydrofluoric acids which were converted into a wide variety of other chemicals. Twenty-eight samples of workroom air were taken for periods ranging from 10 to 30 minutes with midget impingers equipped with prefilters to exclude particulate matter. This was done using 0.005 N sodium hydroxide as the absorbing fluid. Hydrofluoric acid concentrations ranged from 0.07 to 10 ppm (0.06-8.2 mg HF/cu m) with a mean of 1.03 ppm (0.85 mg HF/cu m). The major sources of hydrogen fluoride were reported to be the firing kilns and process equipment leaks. Recommended controls included installation of hoods on kilns vented to an ammonia-water scrubber; frequent inspections of process equipment, especially valves and piping; and expeditious repair of leaks. Evacuation alarms and an automatic hydrogen fluoride sampler had been installed.

(b)   Foundry Operations

In a general discussion of the use of chemicals in foundries, Boddey
[149] reported finding hydrogen fluoride in material volatilized from
exothermic compounds and fluxes. Laboratory tests of low-grade exothermic
compounds, used to decrease the rate of cooling of molten metal, indicated
that 2 g of gaseous material was evolved from a 100-g sample of an
exothermic compound. The gaseous material contained about 70 cc of gaseous
fluorides together with other components. A similar test of a better-grade
exothermic material evolved only about 5 cc of gaseous fluorides.   An
experimental exposure measurement in a crane cab in a foundry was carried
out with the low-grade material used in the first test. The crane cab was
placed in an area of maximum "smoke" exposure above a casting pit where six
17-ton steel ingots were poured in a period of 30 minutes. Each ingot was
treated with 6 kg of the exothermic compound. Under these conditions, 2.6
ppm (2.1 mg/cu m) of gaseous fluorides were found. It was emphasized that
these were not conditions typical of normal exposures.

(c)   Fertilizer and Phosphate Rock Production

In 1954, Poppe [150] reported on industrial hygiene engineering
studies conducted in a number of phosphate rock-acidulating and fertilizer-
blending plants.   The initial study, which took place in 1949, was
undertaken as the result of complaints from people living in   the
neighborhood of the plant who were concerned about the presence of
irritating gases in the community air. The results of this study indicated
the necessity for a more thorough investigation of the industry. Poppe
stated, without giving substantiating data, that hydrogen fluoride and
other acid gases were the air contaminants in acidulating plants. Although

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the results of the air sampling were given in terms of hydrogen fluoride, the sampling method as stated (glass impingers containing distilled water or 0.1 N potassium hydroxide) would sample particulate as well as gaseous fluorides. Therefore, the results would more aptly have been reported as total fluoride. The results of sampling in three phosphate rock-acidulating and four fertilizer-blending plants are shown in Table IV-1.

The reason for the general atmosphere samples being higher than the breathing zone samples was not explained. Poppe concluded that a fluoride health hazard existed. He reported without further details that the working environment at one plant was so intolerable that personnel could not remain with the sampling instruments. The workers had been supplied with respiratory protection of the wrong type, namely, gauze dust masks or respirators with organic vapor cartridges. Other controls, if any, were not described. Broad recommendations were made for training management personnel in the hazards presented by fluorides, for studies of acidulation plants to determine the most effective way to control gaseous fluorides in the plant atmosphere, for provision for proper and adequate respiratory protective devices for acid-plant employees, for studies of blending plants to determine material-handling methods which would generate the least dust, and for dust control by local exhaust ventilation.

Rye [45] in a report of clinical observations of phosphate workers described three operations, two of which produced exposure to gaseous fluorides. The production of phosphate rock produced only dust exposure, while production of phosphoric acid and triple superphosphate (TSP) produced exposures to hydrogen fluoride and other fluoride compounds. Rye stated that engineering controls (not otherwise described) and the fact

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TABLE IV-1

RESULTS OF SAMPLING FOR FLUORIDES IN
ACIDULATING AND BLENDING PLANTS

Operation	Sampling Location	Number of Samples	Average Hydrogen Fluoride Concentrations	
			ppm	mg/cu m
ACIDULATING PLANTS				
Mixing	BZ*	15	6.35	5.21
	GA*	4	7.70	6.31
Cutting	BZ	"	1.18	0.97
	GA	"	2.77	2.27
Conveying	BZ	0	--	--
	GA	2	8.80	7.22
Storage	BZ	0	--	--
	GA	7	14.60	11.97
BLENDING PLANTS				
Storage	BZ	0	--	--
	GA	2	5.90	4.84
Conveying	BZ	1	1.54	1.26
	GA	"	30.90	25.34
Blending	BZ	"	5.90	4.84
	GA	"	25.00	20.50
Packing	BZ	4	19.80	16.24
	GA	0	--	--

*BZ = Breathing Zone
*GA = General Atmosphere

From reference 150

that the plant was open on three sides easily kept airborne concentrations

of fluorides in the phosphoric acid plant below 3 ppm, calculated as

hydrogen fluoride. Although Rye reported that continuous air samples were

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taken in conjunction with control studies, no results of the air sampling were given, except for one 8-hour average exposure at 2.4 ppm of gaseous fluoride. Sampling and analytical methods were not described, nor were the proportions of hydrogen fluoride and silica reaction products determined. In connection with the production of TSP, Rye stated that total airborne concentrations of 2-4 ppm, calculated as hydrogen fluoride, were the rule, but that only 40% of this was in gaseous form. Controls included the wearing of respirators, duty rotation, and enclosure and air-conditioning of the crane cab.

(d)   Welding

Tebbens and Drinker, [151] Jones, [152] and Drinker and Nelson [153] failed to find significant generation of hydrogen fluoride from welding with coated rods containing fluorides. Thrysin et al, [154] also investigating fumes and gases in arc welding with coated rods, found gaseous fluorides ranging from 0.2 to 12.5 mg/electrode. Generally, the amounts of gaseous fluorides tended to increase as higher voltages and amperages were used in arc welding. However, the authors [154] stated that the tests did not demonstrate with any degree of certainty that gaseous fluorine compounds occurred in the fumes during "ordinary welding." They did not give the basis for this statement. On the other hand, Krechniak [155] examined the fumes and gases emitted during welding with automatic machines, which generally use higher amperages. [154] He reported "volatile" (presumably gaseous) fluorine compounds ranging from 0.7 to 2.8 mg/cu m as hydrogen fluoride in the atmosphere at or near welders' stands, while the airborne concentrations of particulate fluorides were considerably less. In an attempt to resolve the apparent discrepancy, the

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reported sampling methods of the various references cited were examined. Tebbens and Drinker [151] filtered the air sample prior to sampling for gaseous fluorides. Jones [152] did not describe his sampling methods. Thrysin et al [154] sampled for gaseous fluorides after removing the particulate matter from the air with an electrostatic precipitator. Krechniak [155] described his sampling method only as air "blown" into polyethylene bottles containing dilute sodium hydroxide. Taken literally, this type of sampling would probably sample for total fluorides, rather than for gaseous fluorides only. The different findings, therefore, could be explainable in terms of different sampling methods, or different test conditions, eg, amperage and voltage. The evidence concerning gaseous fluoride exposure in welding operations appears inconclusive at this point, requiring further investigation for resolution.

(e) Miscellaneous

Feiner and Moskowitz [156] briefly reported health hazards associated with the manufacture of quartz crystals for radio communications equipment. Quartz crystals were cut into wafers which were etched for several minutes in 45% hydrofluoric acid or in a solution of undesignated concentration of ammonium bifluoride. Local exhaust ventilation was reportedly efficient in two plants using hydrofluoric acid. No hydrogen fluoride was detected in a workroom where ammonium bifluoride was used for etching and where good general ventilation was present.

Scott [157] described the use of hydrofluoric acid in the production of printed wiring. The acid was used to produce slots and holes in resin-treated fiberglass boards. No exposure data were given, but recommendations were made for the prevention of skin contact by wearing

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protective clothing and the use of exhaust ventilation for control of acid mist.

The use of hydrofluoric acid in cleaning glass tubing used in the manufacture of neon signs was briefly described by Dickson and Paganini. [158] The authors stated that hydrofluoric or nitric acid was used to remove mercury from old tubing, without protective equipment, and that workers were not aware of the hazards. No exposure data were given. Recommended control measures included protective clothing, first aid, and worker instruction.

An unusual exposure, which was nonindustrial but probably comparable to industrial situations, was the subject of an unpublished report from the Texas State Department of Health (MC Wukasch, written communication, February 1974). A woman complained of a condition in her home which caused itching and tingling of the skin, skin lesions requiring hospitalization, loss of hair, and occasional nausea and vomiting. Similar symptoms afflicted the entire family, including the dog. Other conditions noted were etching of glass articles and rapid deterioration of oil paintings, light bulbs, plastics, and fabrics. Analyses of glass and fabric samples showed high levels of fluoride. Further investigation showed that the cause was hydrogen fluoride formed by thermal decomposition of a fluorocarbon refrigerant leaking from an air conditioner.

Laskin et al [159] mentioned the presence of airborne hydrogen fluoride in the production of beryllium. However, the only exposure data reported involved either particulate or total fluoride concentrations.

Jager [160] in his discussion of hazards in the electroplating industry briefly mentioned the use of hydrofluoric acid as an acid dip for

surface treatment of metals. The baths were operated at temperatures ranging from room temperature to about 93.3 C. The HF acid concentrations used in the baths varied widely, and some baths were operated without current while others used "extremely high" current densities. No exposure data were given, but local exhaust ventilation was recommended for control.

Hydrogen fluoride was listed as a possible contaminant in submarine atmospheres [161] from the decomposition of fluorocarbon passing through the carbon monoxide burner. However, hydrogen fluoride was not included in a list of compounds which had been identified in the submarine atmosphere.

In 1924, Salls [162] briefly described hydrogen fluoride usage in the manufacture of opaque glassware. High airborne workplace concentrations of HF were indicated by etching of windows and of the glass front of a clock. Exposure data were not obtained, but the discharge of HF acid vapor into the room was "practically eliminated" when the concentration of HF acid in "the bath" was reduced and a "neutral component" was added.