criteria for a recommended standard....

OCCUPATIONAL EXPOSURE
TO
HYDROGEN FLUORIDE

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Center for Disease Control
National Institute for Occupational Safety and Health

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PREFACE

The Occupational Safety and Health Act of 1970 emphasizes the need for standards to protect the health and safety of workers exposed to an ever-increasing number of potential hazards at their workplace. The National Institute for Occupational Safety and Health has projected a formal system of research, with priorities determined on the basis of specified indices, to provide relevant data from which valid criteria for effective standards can be derived. Recommended standards for occupational exposure, which are the result of this work, are based on the health effects of exposure. The Secretary of Labor will weigh these recommendations along with other considerations such as feasibility and means of implementation in developing regulatory standards.

It is intended to present successive reports as research and epidemiologic studies are completed and as sampling and analytical methods are developed. Criteria and standards will be reviewed periodically to ensure continuing protection of the worker.

I am pleased to acknowledge the contributions to this report on hydrogen fluoride by members of my staff and the valuable constructive comments by the Review Consultants on Hydrogen Fluoride, by the ad hoc committees of the American Academy of Occupational Medicine and the Society for Occupational and Environmental Health, and by Robert B. O'Connor, M.D., NIOSH consultant in occupational medicine. The NIOSH recommendations for standards are not necessarily a consensus of the consultants and professional societies that reviewed this criteria document on hydrogen fluoride. Lists of the NIOSH Review Committee members and of the Review Consultants appear on the following pages.

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The Division of Criteria Documentation and Standards Development, National Institute for Occupational Safety and Health, had primary responsibility for development of the criteria and recommended standard for hydrogen fluoride. University of Washington, School of Public Health and Community Medicine developed the basic information for consideration by NIOSH staff and consultants under contract No. HSM-99-73-36. Patricia G. Heitman had NIOSH program responsibility and served as criteria manager.

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CRITERIA DOCUMENT: RECOMMENDATIONS FOR AN OCCUPATIONAL EXPOSURE STANDARD FOR HYDROGEN FLUORIDE

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I. RECOMMENDATIONS FOR A HYDROGEN FLUORIDE STANDARD

The National Institute for Occupational Safety and Health (NIOSH) recommends that worker exposure to hydrogen fluoride be controlled by requiring compliance with the following sections. The standard is designed to protect the health and safety of workers for up to a 10-hour workday, 40-hour workweek over a working lifetime. Compliance with all sections of the standard should prevent adverse effects of exposure to hydrogen fluoride in the workplace. The hydrogen fluoride standard is measurable by techniques that are valid, reproducible, and available to industry and government agencies. Sufficient technology exists to permit compliance with the recommended standard. The standard will be subject to review and revision as necessary.

"Hydrogen fluoride" is defined as:

(a) Gaseous or liquified anhydrous hydrogen fluoride and aqueous solutions thereof (hydrofluoric acid). The abbreviations HF and HF acid, as used in this document, denote the anhydrous and aqueous forms, respectively.

(b) Any gaseous fluoride which is a byproduct of processes using or producing hydrogen fluoride as defined above and is emitted into the air concomitantly with HF or HF acids.

"Occupational exposure to hydrogen fluoride" is defined as exposure to HF at airborne concentrations at or above one-half the recommended time-weighted average (TWA) environmental limit.

Section 1 - Environmental (Workplace Air)

(a) Occupational exposure shall be controlled so that no worker is exposed to hydrogen fluoride at a TWA concentration greater than 2.5 milligrams of fluoride ion (atomic weight 19) per cubic meter of air (2.5 mg F/cu m) for up to a 10-hour workday, 40-hour workweek, or greater than a ceiling of 5.0 milligrams of fluoride ion per cubic meter of air (5.0 mg F/cu m) as determined by a sampling time of 15 minutes. If both particulate and gaseous fluorides are present, total fluoride exposure from all occupational sources shall not exceed the recommended TWA concentration. Control of occupational exposure to any particulate inorganic fluorides produced as a byproduct or an end product of the use or production of HF shall be governed by the criteria document, Occupational Exposure to Inorganic Fluorides.

(b) Sampling and Analysis

Procedures for sampling air for HF, calibration of equipment, and analysis of samples shall be as provided in Appendices I and II, or by any method shown to be equivalent in precision, accuracy, and sensitivity to the methods specified.

Section 2 - Medical

Medical surveillance shall be made available as specified below for all workers subject to occupational exposure to hydrogen fluoride.

(a) Preplacement examination shall include as a minimum:

(1) Medical and occupational histories to elicit data on worker exposure to hydrogen fluoride and inorganic fluorides and evidence

of respiratory and renal diseases.

(2) A judgment of the worker's physical ability to use negative or positive pressure respirators as defined in 29 CFR 1910.134.

(3) A urinalysis to determine the preexposure fluoride concentration in urine and to test for renal function.

(4) Examination of the skin and corneas for the presence of scars.

(5) An X-ray of the pelvis on all male workers (see chapter V, Radiologic Examination). Special shielding of gonads shall be provided during radiography. The physician evaluating all X-ray films shall be made aware of the fluoride exposure of the worker and shall have knowledge of the radiologic signs of osteofluorosis.

(6) A worker with evidence of renal disease, impaired pulmonary function, scarring of the skin or cornea, or osteofluorosis shall be evaluated by a physician and, if appropriate, informed of the possibility of an increased health risk resulting from exposure to HF.

(b) Periodic Examination

(1) X-ray of the pelvis of males shall be considered by the examining physician when the average of preshift urinary fluoride concentrations for the preceding 6 years exceeds 4.0 mg F/liter.

(2) Urinalysis, skin and cornea examination, and X-ray of the pelvis of males, if not already conducted, shall be offered to presently employed workers within 6 months of the promulgation of a standard incorporating these recommendations.

(3) Any worker occupationally exposed to hydrogen fluoride and exhibiting signs or symptoms of respiratory tract irritation shall be

examined by a physician and shall have follow-up chest X-rays taken and pulmonary function tests performed as considered necessary by the examining physician.

(4) Workers with eye complaints following exposure to hydrofluoric acid shall have follow-up visual acuity tests and an ophthalmological examination as necessary.

(5) Any worker whose skin comes in contact with hydrofluoric acid shall receive prompt medical attention.

(c) Biologic Monitoring

Postshift F urinalysis shall be made available at intervals not exceeding 3 months to at least one-fourth of all workers with occupational exposure to hydrogen fluoride. The employer shall ensure that each exposed worker has the opportunity of receiving an F analysis of his urine every year. Spot urine samples shall be collected at the conclusion of the workshift after 4 or more consecutive days of exposure. Urinary preshift F analysis shall be made available to all exposed workers at least annually. Preshift spot samples shall be collected at the start of the workshift at least 48 hours after the last occupational exposure. Results shall be calculated to a specific gravity of 1.024. Urine specimens with a specific gravity less than 1.010 shall be discarded and another specimen obtained. Procedures for sampling and analysis shall be as described in Appendix II or by any other procedure equivalent in precision and accuracy. If an individual's postshift urinary F level exceeds 7.0 mg/liter, preshift spot urine samples for analysis shall be collected within 2 weeks at the start of a workshift at least 48 hours after a previous occupational exposure and a repeat postshift spot sample for analysis shall be collected at the conclusion of the workshift. This shall be done at the end of the workweek in which the preshift sample is collected. If the F level of the second sample is above either the preshift limit of 4.0 mg/liter or the postshift limit of 7.0 mg/liter, steps shall be taken to evaluate dietary sources, personal hygiene, basic work practices, and environmental controls.

If the group (job classification) median postshift urinary F levels exceed 7.0 mg/liter, the working environment shall be evaluated through an industrial hygiene survey and steps shall be taken to ensure compliance with the environmental limit. Urinary F analyses shall be performed monthly until the cause of elevated urinary F has been corrected as demonstrated by a return of the group median to a postshift value not exceeding 7.0 mg/liter. The primary methods of control will be engineering and work practices. Use of administrative controls for the individual or group can also be considered.

(d) Medical Records

All pertinent medical records including all information regarding biologic determinations shall be maintained at least 20 years after the individual's employment is terminated. These records shall be available to the medical representatives of the Secretary of Labor, of the Secretary of Health, Education, and Welfare, of the employer, and of the employee or former employee at his request.

Section 3 - Labeling (Posting)

(a) Containers of anhydrous hydrogen fluoride shall bear the following label in addition to, or in combination with, labels required by other statutes, regulations, or ordinances:

DANGER!
HYDROGEN FLUORIDE, ANHYDROUS
EXTREMELY HAZARDOUS LIQUID AND GAS
SEVERE INHALATION, SKIN, AND EYE HAZARD
CAUSES BURNS
DO NOT BREATHE GAS
DO NOT GET IN EYES, ON SKIN, ON CLOTHING

In case of contact, immediately flush skin or eyes with water continuously, remove contaminated clothing, and continue flushing until medical attention is obtained.

CYLINDER HANDLING AND STORAGE

Keep away from heat.
Protect from damage.
Do not wash out empty cylinders with water.
Be sure connections are tight, check for leaks.
Loosen closure carefully, keep sources of ignition away.
Wear respiratory protection and protective clothing when connecting, disconnecting, or opening valve.
Do not use cylinder valve for control; connect to needle valve.

(b) Containers of aqueous hydrogen fluoride (hydrofluoric acid) more concentrated than 40% shall bear the following label in addition to, or in combination with, labels required by other statutes, regulations, or ordinances:

DANGER!
HYDROFLUORIC ACID
EXTREMELY HAZARDOUS LIQUID AND GAS
LIQUID CAUSES BURNS
SEVERE INHALATION, SKIN, AND EYE HAZARD
AVOID BREATHING GAS
AVOID CONTACT WITH SKIN, EYES, AND CLOTHING

In case of contact, immediately flush skin or eyes with water continuously, remove contaminated clothing, and continue flushing until medical attention is obtained.

HANDLING AND STORAGE

Before moving containers, be sure closure is securely fastened.
Store with closure up.
Vent regularly to release pressure, avoid sources of ignition while venting; wear respiratory, skin, and eye protection.
Release pressure carefully.
Avoid damage to containers.
Keep out of direct rays of sun, away from heat.
Do not wash out containers with water.
In case of spillage, neutralize; then flush with water.

(c) Containers of hydrofluoric acid of 40% or less concentration shall bear the following label in addition to, or in combination with, labels required by other statutes, regulations, or ordinances:

DANGER!
HYDROFLUORIC ACID
HAZARDOUS LIQUID
CAUSES SEVERE BURNS WHICH MAY NOT BE IMMEDIATELY PAINFUL OR VISIBLE
AVOID CONTACT WITH EYES, SKIN, CLOTHING

In case of contact, immediately flush skin or eyes with water, remove contaminated clothing, and continue flushing until medical attention is obtained.
In case of spillage, neutralize; then flush with water.

(d) The following warning sign shall be affixed in a readily visible location at or near entrances to areas where hydrogen fluoride is stored, handled, or used in industrial processes, excluding nonroutine laboratory use, and in which there is a potential for emergencies involving uncontrolled release of hydrogen fluoride. This sign shall be printed both in English and in the predominant language of non-English-speaking workers. All employees shall be trained and informed of the hazardous areas, with special instruction given to illiterate workers.

DANGER!
HYDROGEN FLUORIDE HAZARD AREA
UNAUTHORIZED PERSONS KEEP OUT

Prior to entry, contact (employer-designated person).
Entry prohibited without permit and specified protective clothing.

SEVERE SKIN AND EYE HAZARD--CAUSES BURNS

In emergency, do not enter without complete respiratory
protection and protective clothing, located at
(specific locations to be supplied by employer).

(e) Hydrogen fluoride hazard areas required to be posted in accordance with Section 3(d) shall be clearly delineated by an appropriate boundary, such as a wall with a door for controlled entry, a raised curb sufficient to contain spills and painted a distinctive color, or a painted line of a distinctive color.

(f) All hydrogen fluoride systems, piping, and associated equipment, shall be plainly marked for positive identification in accordance with American National Standard A13.1-1975. Shut-off valves and switches shall be conspicuously labeled. Hydrogen fluoride cylinders in use shall be plainly marked "in use" to distinguish them from those not in use.

(g) All protective clothing, safety equipment, tools, and removable equipment, such as motors or pumps, after having been used in association with hydrogen fluoride shall be distinctively marked or colored to warn against use or contact by unprotected personnel.

Section 4 - Personal Protective Equipment

(a) Protective Clothing

(1) Protective clothing impervious to hydrogen fluoride shall be worn when airborne concentrations of hydrogen fluoride may exceed the environmental limits, or when direct contact with HF or HF acid may occur, eg, when closed systems are opened for maintenance, or if leaks are likely to occur. Unless eye protection is afforded by a respiratory hood or facepiece, chemical goggles and face shields shall be worn. Eye and face protective equipment, and its use, shall conform to 29 CFR 1910.133.

(2) In addition to the respiratory protection specified in Table I-1, personnel performing operations where escape of liquid or gaseous anhydrous hydrogen fluoride may occur, or performing emergency operations involving exposure to liquid or gaseous anhydrous hydrogen fluoride or exposure to sprays of aqueous hydrofluoric acid shall wear impervious gloves, boots, and a continuous-flow, air-supplied impervious full-body suit with auxiliary self-contained air supply, or an impervious full-body suit and self-contained positive pressure full facepiece breathing apparatus. If unventilated suits are worn, stay time in the work area shall be limited with due consideration of the heat stress factors involved. An adequate supply of such protective clothing shall be kept available for emergencies.

(3) Sleeves of protective clothing shall be tight at the wrists and worn over gloves or gauntlets. Trouser legs shall be worn over boot tops.

(4) Protective clothing specifically used for hydrogen fluoride protection shall be marked distinctively, preferably with a distinctive color, to differentiate it from other protective clothing.

(5) The employer shall designate a person to be in charge of posted hydrogen fluoride hazard areas. This person shall specify, in accordance with the provisions of this standard, the protective clothing required in his area of responsibility.

(6) Hydrogen fluoride protective clothing shall be basified with sodium hydrogen carbonate, washed, dried, and inspected for integrity after each use, and immediately prior to reissue. Gloves shall be inspected for pinholes.

(7) A written procedure shall be established and enforced for the sequential removal of protective clothing in such a manner as to prevent skin contact with hydrogen fluoride. A recommended procedure is:

> Wash gloves, aprons, boots, or jackets and trousers (outer garments) with water.
> Remove mask, hood, or face shield while gloves are still on; wash with water.
> Remove aprons, jacket, trousers, boots, gloves--in that order.
> Wash hands with water, remove goggles, and wash.

(8) Where complete protective clothing is required, a change house, with separate entrances for clean and contaminated personnel, shall be provided. Lockers shall be provided for street clothing. The requirements of 29 CFR 1910.141 shall be met.

(9) The employer shall supply all required protective clothing and shall be responsible for maintaining it in a clean, sanitary, and functional condition.

(b) Respiratory Protection

Engineering controls shall be used wherever feasible to maintain airborne hydrogen fluoride concentrations at or below those recommended in Section 1 above. Compliance with the permissible exposure limits by the use of respirators is only allowed when airborne hydrogen fluoride concentrations are in excess of either workplace environmental limit while required engineering controls are being installed or tested, when nonroutine maintenance or repair is being accomplished, or during emergencies. When a respirator is thus permitted, it shall be selected and used in accordance with the following requirements:

(1) For the purpose of determining the type of respirator to be used, the employer shall measure, when possible, the airborne concentration of hydrogen fluoride in the workplace initially and thereafter whenever process, worksite, climate, or control changes occur which are likely to increase the airborne concentration of hydrogen fluoride.

(2) The employer shall ensure that no worker is overexposed to hydrogen fluoride because of improper respirator selection, fit, use, or maintenance.

(3) A respiratory protection program meeting the requirements of 29 CFR 1910.134 which incorporates the American National

Standard Practices for Respiratory Protection Z88.2-1969 shall be established and enforced by the employer.

(4) The employer shall provide respirators in accordance with Table I-1 and shall ensure that the employee uses the respirator provided.

(5) Respiratory protective devices described in Table I-1 shall be those approved under the provisions of 30 CFR 11.

(6) The employer shall ensure that employees are instructed on the use of respirators assigned to them and on how to test for leakage.

(7) Each area required to be posted in accordance with Section 3(d) shall have at least two emergency respirators and two sets of protective clothing readily available in nearby locations which do not require entry into a contaminated atmosphere for access. Each set shall consist of at least two self-contained breathing apparatus, full-facepiece pressure-demand type, and the protective clothing specified for emergencies in Section 4(a)(2) of this standard.

(8) Respirators specified for use in atmospheres of higher concentrations of hydrogen fluoride may be used in atmospheres of lower concentrations.

(9) The employer shall ensure that respirators are cleaned, maintained, and stored in accordance with 29 CFR 1910.134, as currently amended.

(10) Canisters shall be discarded after use or whenever an odor or taste is detected, and replaced with fresh canisters. Unused canisters shall be discarded and replaced when the seal is broken or at the expiration of the shelf life as recommended by the manufacturer.

TABLE I-1

RESPIRATOR SELECTION GUIDE FOR PROTECTION AGAINST HYDROGEN FLUORIDE

Multiples of TWA Limit	Respirator Type
Less than or equal to 10X	(1) Full-face gas mask, chest- or back-mounted type, with industrial size hydrogen fluoride or acid-gas canister (2) Chemical cartridge respirator with full facepiece and cartridge(s) and filter(s) providing protection against hydrogen fluoride (3) Type C supplied-air respirator, demand or pressure-demand type (negative or positive pressure), with full facepiece, hood, or helmet with shroud
Less than or equal to 100X	Combination respirator which includes a Type C supplied-air respirator, pressure-demand or other positive pressure or continuous-flow type with full facepiece and an auxiliary self-contained breathing apparatus, pressure-demand or other positive pressure type
Greater than 100X	(1) Self-contained breathing apparatus with full facepiece, pressure-demand or other positive pressure type (2) Continuous-flow air-supplied suit with auxiliary self-contained breathing apparatus, pressure-demand or other positive pressure type.

TABLE I-1 (CONTINUED)

RESPIRATOR SELECTION GUIDE FOR PROTECTION AGAINST HYDROGEN FLUORIDE

Multiples of TWA Limit	Respirator Type
Emergency situations (No concentration limit)	(1) Self-contained breathing apparatus with full facepiece, pressure-demand or other positive pressure type (2) Continuous flow air-supplied suit with auxiliary self-contained breathing apparatus, pressure-demand or other positive pressure type
Evacuation or escape	(1) Self-contained breathing apparatus with full facepiece. (2) Full-face gas mask, front or back mounted type, with industrial-size hydrogen fluoride or acid-gas canister

Section 5 - Informing Employees of Hazards from Hydrogen Fluoride

At the beginning of employment, workers whose jobs may involve exposure to HF at airborne concentrations greater than one-half the TWA limit, or who will work in areas required to be posted in accordance with Section 3(d) shall be informed of the hazards, symptoms of overexposure, emergency procedures, and precautions to ensure safe use and to minimize exposure. First-aid procedures shall be included, with emphasis on the importance of prompt, copious, and continuous irrigation of eyes and skin, despite initial lack of pain. The information shall be posted in the work area and kept on file, readily accessible to the worker.

A continuing education program, conducted by a person or persons qualified by reason of experience or special training, shall be instituted to ensure that all workers have current knowledge of job hazards, first-aid procedures, maintenance procedures, and cleanup methods, and that they know how to use respiratory protective equipment and protective clothing. Retention of this information by workers in areas required to be posted in accordance with Section 3(d) shall be verified by drills simulating emergency situations appropriate to the work situation, held at intervals not exceeding 6 months. Drills should cover, but should not be limited to, the following:

Evacuation procedures.

Handling of spills and leaks, including decontamination.

Location and use of emergency firefighting equipment.

First-aid and rescue procedures.

Location, use, and care of protective clothing and respiratory protective equipment.

Location of shutoff valves or switches.

Location, purpose, and use of safety showers, eyewash fountains, and other sources of water for emergency use.

Operating procedures.

Entry procedures for confined spaces.

Prearranged procedures for obtaining emergency medical care.

Information, as required, shall be recorded on the "Material Safety Data Sheet" shown in Appendix III or on a similar form approved by the Occupational Safety and Health Administration, US Department of Labor.

Section 6 - Work Practices

(a) Emergency Procedures

For all work areas in which there is a potential for emergencies, procedures as specified below, as well as any other procedures appropriate for a specific operation or process, shall be formulated in advance and employees shall be instructed and drilled in their implementation.

(1) Procedures shall include assignment of individual or team responsibilities and prearranged plans for:

(A) Immediate evacuation of workers with signs or symptoms of adverse effects due to hydrogen fluoride overexposure.

(B) Transportation of injured workers.

(C) Any necessary calls, such as alerting medical facilities of the impending arrival of injured workers, and calls to suppliers or manufacturers of hydrogen fluoride for assistance.

(D) Designation of medical receiving facilities and names of physicians trained in hydrogen fluoride emergency procedures.

(2) Approved eye, skin, and respiratory protection as specified in Section 4 shall be used by personnel essential to emergency operations.

(3) Nonessential employees shall be evacuated from exposure areas during emergencies. Perimeters of areas of hazardous exposure shall be defined, posted, and secured.

(4) Personnel who cannot be evacuated shall keep upwind of spills or leaks, if possible. Personnel properly trained in the procedures and adequately protected against the hazards shall shut off sources of hydrogen fluoride, neutralize and clean up spills, and repair leaks as

quickly as possible. Supplies of lime or soda ash shall be readily available for neutralizing spills. Sources of water shall be available for washdown of spills.

(5) Water used to flush areas contaminated with hydrogen fluoride shall be impounded and guarded until neutralized. Water used to absorb hydrogen fluoride shall only be discharged to municipal sewers or drains, if it is adequately diluted or otherwise treated to meet applicable local, state, or federal discharge and water pollution regulations.

(6) In case of fire, hydrogen fluoride sources shall be shut off or removed. Cylinders shall be removed to a safe place or cooled with water. Water may be used for fighting fires involving hydrogen fluoride.

(7) Hydrogen fluoride in contact with skin or eyes must be removed by prompt, copious, and continuous washing with water until medical attention is obtained. Contaminated clothing shall be removed immediately. If hydrogen fluoride is inhaled, the victim shall be removed to an uncontaminated atmosphere, given artificial respiration, if required, and provided with immediate medical attention.

(b) Control of Airborne Hydrogen Fluoride

(1) Engineering controls, such as process enclosure or local exhaust ventilation, shall be used to maintain airborne hydrogen fluoride concentrations within the recommended limits. Ventilation systems shall be designed to prevent the accumulation or recirculation of hydrogen fluoride in the workroom and to remove hydrogen fluoride from the breathing zones of workers. Ventilation systems and equipment shall be constructed of materials resistant to corrosion by hydrogen fluoride and shall be

equipped with condensate drip safeguards. Exhaust discharged to outside air from ventilation systems must conform to applicable local, state, and federal air pollution regulations. Ventilation systems shall be subject to regular preventive maintenance and cleaning to ensure maximum effectiveness, which shall be verified by periodic airflow measurements. Adequate tempered makeup air shall be provided to workrooms in which exhaust ventilation is operating.

(2) Ventilation for electroplating or other open surface tanks containing solutions of hydrogen fluoride or generating hydrogen fluoride shall conform to the requirements of 29 CFR 1910.94.

(3) Ventilation of welding operations involving fluxes which generate hydrogen fluoride shall conform to the requirements of 29 CFR 1910.252, as currently amended.

(4) General ventilation shall be provided for all enclosed areas where anhydrous hydrogen fluoride containers or systems are located, where 40% or more concentrated aqueous hydrofluoric acid is stored, handled, used, or in transit. Relative positions of air inlets and outlets shall be located to provide uniform cross-ventilation without short circuits or dead spots. Switches for ventilation equipment shall be located outside the hydrogen fluoride area and shall be equipped with lights to indicate operation. Air outlets for hydrogen fluoride areas shall be located so that contamination of air inlets to any rooms or structures will not result.

(c) Storage

(1) Hydrogen fluoride shall be stored in cool, dry, well ventilated areas out of the direct rays of the sun.

(2) Storage areas shall be surrounded by a distinctively colored curb or barrier sufficient to contain spills and to delineate the hazardous area. Drains leading to neutralizing pits shall be provided for ease of cleanup and washdown. A source of water shall be available. Floors of storage areas shall be acid-resistant and nonporous.

(3) Hydrogen fluoride containers shall be stored with closures up for ease of venting and prevention of leaks. Metal containers shall be vented on receipt and at weekly intervals to release any hydrogen formed by reaction of hydrogen fluoride with containers. Sources of ignition shall be eliminated during the venting operation.

(4) Hydrogen fluoride containers shall be secured to prevent falling, upsetting, or rolling and shall be protected from mechanical damage, heat, and corrosion.

(5) Containers of hydrogen fluoride shall be used on a first-in, first-out basis. Stores of hydrogen fluoride shall be limited in quantity to the minimum amount necessary for the operation. Cylinders should not be stored for more than 4 months; drums should not be stored for more than 90 days.

(6) Cylinders in use shall be plainly marked "in use" to differentiate from those not in use. Empty containers shall be separated from full containers.

(7) Other materials which will react with hydrogen fluoride shall not be stored where contact can occur under uncontrolled conditions.

(8) Containers shall be periodically inspected for leaks and deterioration in accordance with 29 CFR 1910.166.

(9) Under no circumstances shall hydrogen fluoride be stored in glass, fibrous glass-reinforced plastic containers, or other noncompatible materials.

(d) Handling and General Work Practices

(1) Tools and equipment used on hydrogen fluoride containers or systems shall be neutralized where appropriate with 10% soda ash solution, washed, and inspected after each use or before repair. Completion of neutralization shall be verified with indicator paper. If necessary, tools and equipment shall be neutralized, degreased, and again neutralized.

(2) Prompt medical attention shall be obtained for any skin or eye contact with hydrogen fluoride, regardless of how slight.

(3) Returnable hydrogen fluoride containers may not be washed out with water.

(4) Valves and joints in piping carrying hydrogen fluoride shall be provided with deflectors to deflect hydrogen fluoride away from workers in the event of a leak.

(5) Safety valves and vents for hydrogen fluoride equipment shall discharge through absorbers and neutralizers.

(6) All aqueous hydrogen fluoride which cannot be diluted sufficiently to meet local, state, or federal regulations shall be discharged into pits containing sufficient alkaline material (normally soda ash or lime) for neutralization. The neutralization of discharge in such pits shall be assured prior to disposal.

(7) Scrap contaminated with hydrogen fluoride shall be decontaminated before being sold or otherwise disposed of.

(8) Safety showers and eyewash fountains shall be provided in the immediate area where hydrogen fluoride is stored, piped, handled, or used. Safety showers shall be equipped with alarms to indicate their use and to summon assistance.

(9) If cooling water is used in conjunction with hydrogen fluoride equipment, a conductivity cell or equivalent equipment shall be used to indicate any change in pH of the water due to leaking hydrogen fluoride and to prevent inadvertent discharges of contaminated water.

(10) Hydrogen fluoride systems shall be neutralized before being opened for maintenance or repair. Lime-water can be used, followed by testing with indicators to determine completion of neutralization. Workers shall be alerted to the possibility of hydrogen fluoride remaining in slag and scale. Employers shall ensure that repairs are only made on systems not in active use.

(11) Goggles may not be raised or handled with HF contaminated gloves.

(12) Valves and pumps shall be readily accessible. They may not be located in pits or in congested areas.

(13) Valves on hydrogen fluoride cylinders may not be used for flow control; they are intended only for discharge. The discharge line shall include a needle valve for flow regulation.

(14) Heat or direct flame may not be applied to hydrogen fluoride cylinders. When low temperatures reduce the pressure below the necessary pressure for transfer, an inert gas may be introduced to a point not exceeding the design pressure limitation of the cylinder.

(15) Hydrogen fluoride delivery tubes or pipes may not be immersed in other liquids without interposing an adequate trap to prevent the dangers of suckback.

(16) Air pressure may not be used to empty drums of HF acid. Drums shall always be emptied by gravity or by an acid-resistant siphon system with a bulb starter.

(17) Welding and burning on tanks or equipment which have contained hydrogen fluoride shall take place only after such tanks or equipment have been thoroughly neutralized, cleaned, purged, dried, and tested for residual acid and hydrogen.

(18) All hydrogen fluoride equipment including valves, fittings, and connections shall be checked for tightness and good working order. All newly made connections shall be inspected for leaks immediately after hydrogen fluoride is admitted. Required repairs and adjustments shall be promptly made.

(19) Written operating instructions and emergency medical procedures shall be formulated and posted where hydrogen fluoride is handled or used.

(20) When hydrogen fluoride cylinders are not in use, valve protection covers shall be in place. Cylinders shall be moved only with the proper equipment and shall be secured to prevent dropping or loss of control while moving. Slings or magnetic devices shall not be used to move hydrogen fluoride cylinders.

(21) No modification, alteration, or repair of containers and associated valves shall be made, except by the supplier or cylinder manufacturer.

(22) Before hydrogen fluoride is admitted to a system, the system shall be thoroughly cleaned, dried, and tested.

(23) Materials for handling aqueous hydrogen fluoride shall be chosen considering the variation of corrosivity with acid concentration.

(24) No one shall work alone when hydrogen fluoride is first admitted into a newly connected system, or while repairing leaks.

(25) Containers and systems shall be handled and opened with care to avoid sudden release of pressure. Approved eye, skin, and respiratory protection shall be worn while opening, connecting, disconnecting, or venting hydrogen fluoride containers and systems. When opening containers or systems, adequate ventilation shall be available to remove inadvertent discharges of hydrogen fluoride.

(26) Leaks in a hydrogen fluoride system shall be repaired only after the damaged system is disconnected and neutralized. Inadvertent entry of hydrogen fluoride into disconnected containers and systems while repair work is in progress shall be prevented by blanking off hydrogen fluoride supply lines.

(27) Any odor of hydrogen fluoride from a normally closed system or color change noted at piping connections which have been painted with an acid-indicating paint shall be reported to a responsible authority without delay.

(28) Contact lenses shall be prohibited when working with HF or HF acid. When suitable corrective lenses cannot be obtained without the use of contact lenses, protective goggles shall be worn.

(e) Work Areas

(1) Where hydrogen fluoride is used or handled, eyewash fountains and safety showers with quick-acting valves shall be located immediately outside the hydrogen fluoride area. They shall be readily accessible in case of emergency, and shall be frequently inspected and kept in good working order.

(2) Hydrogen fluoride hazard areas required to be posted in accordance with Section 3(d) shall be isolated from other work areas insofar as is practicable. They shall be delineated by an appropriate boundary. Entry shall be controlled by a permit system and required passage through a control point. An employer-designated person shall be responsible for approving the permit for entry.

(3) Floors shall be constructed of nonporous acid-resistant materials and shall slope toward drains leading to neutralizing pits.

(4) Electrical equipment shall be explosion-proof in areas where hydrogen fluoride in contact with metals may generate hydrogen.

(5) Shutoff valves and switches shall be conspicuously marked, and employees shall be familiarized with their use. Accesses to shutoff valves shall be kept unobstructed.

(6) Exits from enclosed areas required to be posted in accordance with Section 3(d) shall be plainly marked. Emergency exit doors shall be conveniently located and shall open into areas which will remain free of contamination in an emergency.

(f) Confined Spaces

(1) Entry into confined spaces such as tanks, pits, tank cars, and process vessels which have contained hydrogen fluoride shall be

controlled by a permit system. Permits shall be signed by an authorized employer representative, certifying that preparation of the confined space, precautionary measures, and personal protective equipment are adequate, and that prescribed procedures will be followed.

(2) Confined spaces which have contained hydrogen fluoride shall be inspected and tested for oxygen deficiency, hydrogen, hydrogen fluoride, and other contaminants and thoroughly ventilated, cleaned, neutralized, and washed, as necessary, prior to entry.

(3) Inadvertent entry of hydrogen fluoride into the confined space while work is in progress shall be prevented by disconnecting and blanking off hydrogen fluoride supply lines.

(4) Confined spaces shall be ventilated while work is in progress to keep any hydrogen fluoride concentration below the standard, and to prevent oxygen deficiency and build-up of hydrogen.

(5) Individuals entering confined spaces where they may be exposed to hydrogen fluoride shall be equipped with the necessary personal protective equipment and a lifeline tended by another worker outside the space who shall also be equipped with the necessary protective equipment.

(g) Enclosed Spaces

Enclosed spaces (rooms, buildings, etc) which ordinarily are safe to enter, but which, due to the failure of a system inside, could contain hazardous concentrations of hydrogen fluoride, should have a continuous automatic monitor set to sound an audible alarm inside and outside the enclosed space if hydrogen fluoride concentrations exceed the recommended ceiling. In such areas where concentrations of HF are not known to be safe, the enclosed space shall be entered only if the worker is under observation by a co-worker and if the worker is wearing a respirator suitable for escape.

Section 7 - Sanitation Practices

(a) Plant sanitation shall meet the requirements of 29 CFR 1910.141.

(b) Good personal hygiene shall be encouraged. Hands, arms, and face shall be thoroughly washed prior to eating and at the end of the shift. Facilities shall be provided for this purpose in conformance with 29 CFR 1910.141(d).

(c) Food storage, preparation, and dispensing (even from vending machines), as well as eating shall be prohibited in areas where occupational exposure to hydrogen fluoride may occur. Drinking, smoking, and chewing tobacco or gum shall be prohibited in hydrogen fluoride exposure areas. The employer shall furnish an uncontaminated area for these purposes in conformance with 29 CFR 1910.141(g). A source of drinking water protected from contamination should be provided in hot environments.

Section 8 - Monitoring and Recordkeeping Requirements

(a) Monitoring

Each employer who has a place of employment in which hydrogen fluoride may be released into the workplace air shall determine if any employee is occupationally exposed to hydrogen fluoride. This determination shall be made within 6 months of the promulgation of a standard incorporating the recommended limits, and within 30 days after first operation of a production, process, or control change resulting in possible increase in the quantity of hydrogen fluoride released, or when the employer has any reason to suspect that an employee may be occupationally exposed.

An employee shall be designated as occupationally exposed if observations and calculations made by the employer reveal that a potential exposure exists; or if any information, such as measurements of airborne concentrations of HF or the development of HF-related clinical signs or symptoms, indicate the possibility of occupational exposure; or if the employer has been advised in writing by the Occupational Safety and Health Administration (OSHA) or the National Institute for Occupational Safety and Health (NIOSH) that employees have been occupationally exposed.

If an employee is designated as being occupationally exposed, the employer shall design and implement a monitoring program which shall measure the airborne HF concentration to which the employee is exposed.

An employee's TWA exposure shall be obtained from the results of a single 8-hour sample of airborne HF, or a series of short-period samples which represent the worker's average exposure over an 8-hour work shift. At the same time that a TWA exposure is determined, the employee's peak exposure will be obtained from the results of 15-minute samples taken during periods of expected highest exposure in order to ascertain whether the ceiling limit has been exceeded. In all monitoring, samples representative of the exposure in the breathing zone of the employee shall be collected. Where more than one occupationally exposed employee works at a specific process or operation location, an adequate number of samples shall be collected to permit construction of a TWA exposure and peak exposure for the operation or process. Variations in work and production schedules shall be considered when samples are collected. The minimum number of representative TWA exposure determinations for an operation or process shall be based on the number of workers exposed as provided in Table I-2, or as otherwise indicated by a professional industrial hygienist.

If an employee monitoring program measurement reveals that an employee is occupationally exposed, but not exposed in excess of the recommended environmental limit, the exposure of that employee shall be measured at least once every 6 months.

If an employee monitoring program measurement reveals that an employee is exposed in excess of the recommended environmental limit, the employee shall be notified, control measures required by Section 6(b) shall be initiated, and monitoring shall continue until the adequacy of the control measures has been demonstrated.

If an employee monitoring program measurement reveals that an employee is not occupationally exposed, and if the next consecutive employee monitoring program measurement made not less than 5 working days later supports this finding, the employee monitoring program may be terminated for that employee.

Monitoring shall also be performed when biologic monitoring of an occupationally exposed individual reveals urinary fluoride excretion above the postshift standard of 7.0 mg/liter, adjusted for specific gravity, or when the average postshift urinary F excretion of an exposed group (job classification) exceeds 7.0 mg F/liter, adjusted for a specific gravity of

TABLE I-2

SAMPLING SCHEDULE

Number of Employees Exposed	Minimum Number of Employees Whose Individual Exposures Shall Be Determined
1- 20	50% of the total number of workers
21-100	10 plus 25% of the excess over 20 workers
Over 100	30 plus 5% of the excess over 100 workers

1.024. Monitoring of the work environment in response to a high postshift urinalysis should be conducted on the same day as the required repeat postshift urinalysis (Section 2), and 2-4 hours prior to the repeat analysis to enable correlation of the airborne concentration of HF with the urinary F concentration. Follow-up biologic monitoring shall be performed as specified in Section 2 of this standard.

(b) Recordkeeping

Employers shall maintain records of accidental hydrogen fluoride release requiring evacuation and results of all exposure measurements, environmental surveys, medical examinations, and biologic monitoring. Records shall be maintained so that exposure information is available for individual employees and shall indicate the type of personal protective devices, if any, in use at the time of sampling. Each employee shall be able to obtain information on his own environmental exposure. Such records shall be maintained for at least 20 years after the individual's employment is terminated.

II. INTRODUCTION

This report presents the criteria and the recommended standard based thereon which were prepared to meet the need for preventing occupational diseases arising from exposure to hydrogen fluoride. The criteria document fulfills the responsibility of the Secretary of Health, Education, and Welfare, under Section 20(a)(3) of the Occupational Safety and Health Act of 1970 to "...develop criteria dealing with toxic materials and harmful physical agents and substances which will describe....exposure levels at which no employee will suffer impaired health or functional capacities or diminished life expectancy as a result of his work experience."

NIOSH, after a review of data and consultation with others, formalized a system for the development of criteria upon which standards can be established to protect the health of workers from exposure to hazardous chemical and physical agents. It should be pointed out that any criteria and recommended standard should enable management and labor to develop better engineering controls resulting in more healthful work environments and that mere compliance with the recommended standard should not be used as a final goal.

Hydrogen fluoride is a versatile material with interesting properties. Its catalytic activity in polymerization reactions has resulted in increasing usage in petroleum refining and alkylation processes. Hydrogen fluoride is an important intermediate, for example, in the manufacture of refrigerants and propellants, atomic energy feed materials, aluminum fluoride, and cryolite. Its reactivity is useful in the production of inorganic and organic fluorine-containing compounds. Its physical properties facilitate handling in industrial processes as a liquid or gas, or as an aqueous solution. Its distinctive and irritating odor provides indication of potential exposure situations. It causes serious skin and tissue damage on contact, even in very dilute solutions or low concentrations in air.

These criteria for the standard for hydrogen fluoride are in a continuing series of criteria developed by NIOSH. The proposed standard applies only to the processing, manufacture, handling, and use of hydrogen fluoridey as applicable under the Occupational Safety and Health Act of 1970.

The standard was not designed for the population at large, and any extrapolation beyond occupational exposures is not warranted. It is intended to (1) protect against injury from hydrogen fluoride, (2) be measurable by techniques that are valid, reproducible, and available to industry and official agencies, and (3) be attainable with existing technology.

III. BIOLOGIC EFFECTS OF EXPOSURE

Extent of Exposure

Anhydrous hydrogen fluoride is a colorless liquid or gas which fumes in moist air and has a pungent irritating odor. Its aqueous solutions are also colorless, and fume above a concentration of 40-48%. [1,2] It is manufactured by allowing sulfuric acid to react with acid-grade fluorspar (97% calcium fluoride) in heated rotary or stationary kilns. Hydrogen fluoride is evolved as a gas, purified, and then condensed as liquid anhydrous hydrogen fluoride. [3] Apposite properties are presented in Table XII-1. [2,4,5]

A comparison of the properties of hydrogen fluoride with those of other hydrogen halides indicates deviations from expected values because of polymerization of the hydrogen fluoride molecule. [6-8] The degree of polymerization varies depending on the partial pressure of the hydrogen fluoride and the temperature. At workplace airborne concentrations of HF at or near the recommended limits, the partial pressure will be low enough that negligible polymerization of HF will occur. [9] In this situation, it is probable that the molecular weight of hydrogen fluoride is 20. To account for any uncertainty in this figure, the environmental limits are expressed in mg/cu m instead of in ppm. [10,9] When airborne HF concentrations are converted from ppm to mg/cu m in this document, it is assumed that airborne HF exists as a monomer.

Hydrogen fluoride was first prepared by Margraff in 1768 and was characterized by Scheele in 1771. [11] Between 1876 and 1931, considerable quantities of aqueous hydrofluoric acid were produced and used for cleaning sand from castings and for etching glass. [12] In 1931, anhydrous hydrogen fluoride was first produced commercially. [12] The use of anhydrous hydrogen fluoride as a catalyst in alkylation processes for making high-octane fuel blends began in 1942. [3]

Prior to 1954, the steel industry was the largest consumer of fluorspar from which hydrogen fluoride is generated. Since then, the quantity of fluorspar used for the manufacture of hydrogen fluoride has surpassed that used in the steel industry. [3] In 1958 and 1971, approximately 52% of all fluorspar consumed in the US was used for making hydrogen fluoride. [3,13] Some production figures for hydrogen fluoride are given in Table III-1.

In 1974 production reached 375,000 tons; however, there were no major plans for expansion of hydrogen fluoride production capacity. [16] Currently the major uses of hydrogen fluoride are in the production of cryolite for the aluminum industry, [17] in the manufacture of fluorocarbon compounds, as a

TABLE III-1

HYDROGEN FLUORIDE PRODUCTION

Year	Total production of anhydrous hydrogen fluoride in short tons. Includes that used to make aqueous hydrofluoric acid
1967	161,260
1968	192,265
1969	221,536
1970	224,405
1971	219,481
1972	241,119

Adapted from references 14 and 15

TABLE III-2

1974 HYDROFLUORIC ACID CONSUMPTION

Use	Thousands of Tons
Fluorocarbons manufacture	180
Aluminum (cryolite and aluminum fluoride)	140
Petroleum (alkylate catalysis)	15
Stainless steel	10
Uranium processing	10
Fluoride salts manufacture	15
Miscellaneous (glass etching, electronics, etc)	30

From reference 16

catalyst in alkylation processes, in steel pickling, uranium processing, enamel stripping, glass and quartz etching and polishing, and in various electroplating operations. [18] Consumption of hydrogen fluoride is listed in Table III-2. Hydrogen fluoride is often produced by other industrial processes using fluorides, eg, welding and aluminum production.

Table XII-2 lists some occupations with potential exposure to hydrogen fluoride. NIOSH estimates that 22,000 workers are potentially exposed to hydrogen fluoride in the US.

Effects on Humans

(a) Odor Threshold

Sadilova [19] in 1968 reported the results of odor threshold determinations for hydrogen fluoride using 17 subjects with normal odor perception. The method used was described only as that commonly employed in the Soviet Union. A total of 672 tests were made with concentrations ranging from 0.02 to 0.22 mg HF/cu m. The concentration of HF which was the minimum perceptible for 10 of the 17 subjects was 0.03 mg HF/cu m. For all subjects, the odor threshold ranged from 0.03 to 0.11 mg/cu m.

Lindberg [20] in 1972, using 17 subjects, estimated the threshold of odor for hydrogen fluoride for the "most sensitive persons" (6 people) at a level of 0.04 mg HF/cu m, with the "maximum imperceptible concentration" being 0.02 mg/cu m.

(b) Effects on Skin

Hydrofluoric acid is one of the most corrosive of the inorganic acids. [21] Fluoride ion readily penetrates the skin and travels to deep tissue layers causing liquefaction necrosis of the soft tissues [22-25] and decalcification and corrosion of bone [21,23]. The tissue destruction is accompanied by severe pain, [22-25] which has been attributed by Klauder et al [24] to the calcium precipitating property of the ion which produces immobilization of tissue calcium and a resulting relative excess of potassium in the tissues so that potassium nerve stimulation ensues.

Jones [22] in 1939 described 12 cases of HF acid burns of the skin. One worker received several HF acid burns on the right forearm from 100% hydrofluoric acid. The forearm was immediately soaked in sodium bicarbonate solution, but pain became increasingly severe and the affected area took on a grayish appearance. Pain was almost immediately relieved after calcium gluconate solution was injected into and under all affected areas. Two days later, the burn areas became coagulated and gradually sloughed off during the next 13 days. Complete healing with scar formation occurred in about 1 month.

Another worker [22] splashed 80% HF acid inside his rubber gloves and on his right forearm resulting in whitish discoloration of the skin. Injection of the affected areas with calcium gluconate and application of magnesium oxide paste immediately relieved the pain. Three days after the accident only slight inflammation was evident; this quickly subsided.

Four workers [22] received HF acid burns from a 60% solution in separate accidents. Three were splashed with the acid and one sustained a burn because of a pinhole in the rubber glove worn during the immersion of his hands in the acid solution. The effects of the acid on the skin ranged from mild erythema to tissue destruction. No explanation was offered for the difference in effects. Pain was described as ranging from slight to excruciating. Complete healing of the burns took from 2 to 6 weeks.

In still another case, [22] a laborer with unprotected hands picked up a piece of carbon impregnated with 50% HF acid. Two hours later, his fingertips became extremely painful and the affected skin took on a whitish appearance and became leathery. He was treated by prolonged soaking of the hands in a hot solution of sodium bicarbonate followed by an application of magnesium oxide paste which was reapplied every 4 hours. The persistence of pain for several days indicated that the treatment was unsatisfactory. The skin became necrotic, and dead tissue sloughed off. Over the next 3 months, gradual healing with scar formation occurred. Three other workmen received minor burns from a mixture of hydrofluoric and sulfuric acids of unknown concentrations. These three men experienced mild pain and healing was uneventful. Exposure of two workers to HF acid vapor of unknown concentration resulted in erythema of the face and neck and slight blistering of the lips. The skin inflammation cleared up within 1 day. No respiratory tract irritation was reported in these two cases.

Dale [23] in 1951 described an HF acid burn in a woman employed in the manufacture of glass measuring tubes. Using a 60% aqueous solution of HF, she etched graduations on the measuring tubes. Her right rubber glove became perforated without her knowledge and acid entered the glove. It was about 4 minutes before she experienced pain. The glove was immediately removed and the hand washed in a warm saturated solution of sodium bicarbonate. Magnesium oxide paste was applied and she was taken to the hospital for injection of calcium gluconate into and under the burn. The following day she was in great pain, the hand and fingers were grossly swollen, and the burned skin was white and insensitive. A grey blister which formed on the palm was opened and was found to contain seropurulent fluid. The three medial fingers became necrotic, in some areas down to the bone. A split-skin graft was applied to the palm and the necrotic portions of the fingers were removed. Healing was almost complete 60 days after the accident.

Klauder et al [24] in 1955 described a skin injury in a worker whose fingers came in contact with a 10% HF acid solution. About 1 hour after contact the distal phalanges of both index fingers and thumbs became painful and appeared inflamed and edematous. Later, the affected skin became marble-white. The pain became increasingly severe. Ten cubic centimeters of a 10% solution of calcium gluconate was administered intravenously on two occasions and 1 teaspoon was taken orally three times daily for 4 days. A paste containing calcium gluconate was applied to the injured area. Several days later, part of the epidermis detached, exposing a granulating surface. Complete healing with slight scar formation took place about 1 month after the burn. The authors suggested that the severe pain which characterized the HF acid burn was related to immobilization of calcium resulting in potassium nerve stimulation.

Dibbell et al [25] in 1970 reported three cases of HF acid burns of the skin. A glass-blower sustained a burn of the right index and middle fingers. Approximately 12 hours after the accident, the workman complained of a severe burning sensation. Twenty-four hours later, the skin was blistered, white, and edematous. The white areas were surrounded with an erythematous flair. The burned areas were excruciatingly painful. Necrotic tissue was debrided and the nail of the index finger removed. The edema and erythema subsided rapidly and the burned areas healed satisfactorily during the next 14 days.

Another worker [25] suffered a skin burn when, through a hole in her protective glove, HF acid gained access to the skin of her right thumb. There was a gradual increase of pain and 5 hours after the accident the distal segment of the thumb was tender, white, and edematous. Sixteen days later, she was admitted to a hospital with painful necrosis of the affected area. Healing occurred in 6 weeks. Follow-up examination 2 years later revealed about a 20% loss of the distal thumb pulp.

In 1974, Browne [21] reported that 38 cases of HF splashes and 10 cases of HF vapor burns were treated successfully using calcium gluconate gel. The most extensive skin burn treated with the gel occurred when an employee was splashed with anhydrous HF on the outer side of his right leg affecting an area of about 88 sq in. (570 sq cm). He flushed the area almost immediately with copious amounts of water for 3-4 minutes during which time most of his trousers disintegrated but some fabric remained stuck to the skin. He then applied, within seconds, large quantities of calcium gluconate gel (2.5% calcium gluconate and an antiseptic agent) and kept rubbing it in until additional first aid was received some 10 minutes later. Gel was applied and massaged in until the pain subsided about 1.5 hours later. Healing was virtually complete in 31 days. It was noted that the deep burns were located in those areas where the fabric stuck, creating a barrier through which neither the initial washing nor the gel completely penetrated.

Largent [26] in 1961 reported inhalation studies of HF involving five human subjects, all five being exposed in six separate experiments for 6 hours/day, 5 days/week for 10-50 days at concentrations averaging 1.42-4.74 ppm (1.16-3.89 mg/cu m) and ranging from 0.9 to 8.1 ppm. Exposure at an average concentration of 1.42 ppm (1.16 mg/cu m) ranging from 0.9 to 2.0 ppm (0.7-1.64 mg/cu m) was reported to have no noticeable effect. At concentrations averaging 2.59, 2.72, 3.39, 4.22, and 4.74 ppm (2.12, 2.23, 2.78, 3.46, and 3.89 mg/cu m), the exposed subjects experienced very slight irritation of the face and eyes, and frequent cutaneous erythema was noticed. Flaking of the epithelium, resembling mild sunburn, was reported by one subject after 10 days of exposure. The concentration of HF to which he was exposed averaged 3.39 ppm (2.78 mg/cu m). Application of a face cream to the skin relieved the burning sensation. Irritation and erythema of the face subsided quickly after exposure was terminated.

In summary, the reports presented, [21-26] typical of many cases reported in the world literature, demonstrate that HF and HF acid burns differ from other acid burns in several ways. They cause intense pain which may persist for several days. [22-25] The onset of pain from up to 60% aqueous HF acid solutions may be delayed for several hours. [22,24,25]

The absence of any warning of injury after contact with weaker solutions may result in neglect on the part of the worker to seek prompt first aid. [22,24,25] Hydrofluoric acid solutions stronger than 50-60% and anhydrous HF cause almost immediate pain. [22,23,25] The skin, after contact with HF acid, takes on a blanched appearance, becomes edematous, and may suffer deep extensive destruction of tissue with a tendency to heal slowly. [22-25] Since the degree of tissue destruction not only depends on the concentration of the acid, but also on the duration of contact, immediate irrigation of the affected skin with water is of utmost importance.

Prolonged exposure at airborne HF concentrations averaging as low as 2.59 ppm (2.12 mg/cu m) and ranging from 1.8 to 8.1 ppm (1.5-6.6 mg/cu m) resulted in very mild skin irritation in five out of five human subjects during an experimental study. [26]

(c) Effects on Eyes

Based on the destructive action from skin contamination, one would expect that eye contact with HF acid solutions and anhydrous HF would cause severe and probably permanent damage to the eye, but specific accounts of such injuries were not found in the literature.

McLaughlin [27] in 1946, in reviewing chemical burns of the human cornea, listed two workers having corneal burns from HF acid with prompt healing within 48 hours, and no loss of vision. Details as to the severity of exposure were not given.

Bertuna [28] in 1969 described an eye injury in a 25-year-old man at an alkylation process site who was accidentally exposed to concentrated HF acid spray. Examination of the eyes after profuse water irrigation showed beginning necrosis of the bulbar conjunctivae and practically complete loss of epithelium on the right cornea and partial deepithelization of the left cornea. Five hours after the accident, the patient complained of photophobia and examination revealed marked edema of the eyelids and corneas and intense chemosis. Three days later, the edema of the eyelids was reduced and reepithelization of the corneas occurred. Recovery progressed rapidly, both corneas were completely clear by the thirty-fifth day, and visual acuity returned to normal.

Largent [26] in 1961 noted mild eye irritation in five human subjects exposed to HF at concentrations which averaged 2.59-4.74 ppm (2.12-3.89 mg/cu m) HF during an experimental study. No eye irritation was noticed at concentrations averaging 1.42 ppm (1.16 mg/cu m) and ranging from 0.9 to 2.07 ppm (0.74-1.70 mg/cu m).

(d) Respiratory and Systemic Effects

Burke et al [29] in 1973 reported an unusual case of systemic fluoride poisoning from possible absorption of fluoride through the skin. A 30-year-old laboratory technician was splashed with 100% anhydrous HF on the right side of the face, the neck, and the right arm when a connecting tube ruptured. Within 3-5 minutes, he was placed under the emergency shower and washed for 15 minutes, but he suffered skin burns of the contaminated areas. During the first 24 hours after the accident, he was stuporous, unresponsive to stimuli other than pain, severely nauseated, and he vomited small amounts of brownish, bile-colored fluid. His pulse rate dropped to 48 beats/minute within 6 hours after the accident. Blood pH at this time was 7.21 (normal 7.35-7.45), carbon dioxide combining power was 21.5 mEq/liter (normal 24-30), serum potassium was 6.1 mEq/liter (normal 3.6-5.0). An ECG taken 10 hours after the accident showed slight S-T elevation in lead AVL, V1, V2, and V3, which disappeared within 3 days. Microscopic analysis of the urine on the third day following the accident showed 25 red blood cells, 10 white blood cells, and a few granular and hyaline casts. The urine sediment became normal by the sixth day. The only respiratory symptom was a mild throat irritation during the first hour after the accident. Repeated chest X-rays were all negative. Results of liver and kidney function tests were also normal. Bone and dental X-rays 3 months later revealed no abnormal bone structure. The skin defects at the burn sites required plastic surgery.

The authors [29] estimated that approximately 5 g of HF was spilled on the skin, resulting in second- and third-degree burns over 2.5% of the body surface. The urinary fluoride level 3.5 hours after the accident was 87 mg/liter. During the following 6 hours, it dropped to 56 mg/liter and decreased gradually at a linear rate during the following 2.5 days. The total urine fluoride excretion was calculated to be about 400 mg during the first 3 days after the accident, with 75% excreted within the first 24 hours. Thereafter, F was excreted at a constant daily rate of about 20 mg. The absence of respiratory involvement in this case suggested to the authors that absorption through the skin led to severe systemic fluoride poisoning. Blood samples taken 4 and 10 hours after the accident showed fluoride levels below 0.3 mg/100 ml. The normal blood F concentration may be approximated from the work of Hall et al, [30] who found that the mean serum fluoride concentration in a series of 26 human sera obtained at routine preadmission examinations of subjects entering the hospital for various surgical procedures was 3.7 μg/100 ml. Insofar as the records indicated, none of the patients suffered from chronic renal diseases or overt bone diseases, two types of illness that might have affected serum fluoride concentrations.

Dieffenbacher and Thompson [31] in 1962 reported overexposure to HF in two men employed in a petroleum refinery. One worker was burned on the face, both ears, and areas of the neck by 10% anhydrous HF in propane, which remained on the skin for about 30-35 seconds. He immediately put his head in a tank of "soda bicarb," and shortly thereafter showered thoroughly. Oxygen was administered because of dyspnea, but he died about 2 hours after the accident. Autopsy findings included congestion and hemorrhages in the lower respiratory tract. Both lungs were edematous. There were numerous subepithelial hemorrhages in the kidney pelvises and marked hyperemia of the brain, especially in the white matter of the cerebrum. A few grossly visible, small hemorrhages were found in the posterior portion of the interventricular septum of the heart. Since propane has a very low toxicity, the authors attributed the respiratory changes to pulmonary absorption of HF. While it was speculated that the cardiac changes might also have resulted from HF pulmonary absorption, the cause of the hemorrhages in the kidney pelvises and marked hyperemia of the brain was not discussed. The other workman was blowing out tubes which had contained an oil-HF mixture. Accidentally applied air pressure splashed the material on his chest and under his protective hood, contaminating the left side of the face and neck. Vapors under the hood were strong, and the workman had difficulty in breathing. After taking a shower, he was transferred to a hospital where he was given supportive treatment. Breathing was difficult and on examination, moist rales were heard in both lungs. During the next 12 hours, his breathing improved. Cardiac enlargement, increased bronchiovascular markings, and fluid in the left costophrenic angle were observed by X-ray. By the seventh day, the heart had returned to normal size, but there was still fluid in the left lung base. A 3-day fluoride balance study showed no abnormally high levels of F excretion.

Mayer and Guelich [32] in 1963 reported three accidental deaths from HF exposure. Six workers in two separate accidents were splashed with 70% HF acid. In one accident, four workmen lifted a 20-gallon drum of 70% HF acid to the edge of a vat. When the bung was removed, HF acid was splashed upon all four men. Two men jumped into a nearby vat of water and were unharmed. The other two men lay on the floor and other workmen poured water over them. No safety shower was available. One of these men died 2 hours after the accident from pulmonary edema. The other suffered severe chemical burns, but survived.

In another accident, [32] a 5-pint glass bottle containing 70% HF acid exploded, splashing two workmen with the acid. They were showered and taken to a hospital where they died from pulmonary edema 2 hours after the accident. The authors concluded that the 150-mmHg vapor pressure of HF over a 70% acid solution at 80 F could produce a breathing zone concentration of 10,000-100,000 ppm (8,000-80,000 mg/cu m) in the event that a workman's clothing, particularly in the chest area, became contaminated.

Greendyke and Hodge [33] in 1964 described two accidental deaths from HF overexposure. The two workers were splashed with HF acid when a bottle containing the acid exploded. They were immediately showered and transferred to a distant hospital. On examination, one worker showed no respiratory distress or pain. Burns of various size and degree covered 15% of the body surface. Except for a moist cough and a few wheezes in the chest, he was doing well until sudden respiratory distress occurred about 4 hours after the accident. He died soon afterward. Autopsy findings revealed dilatation of the heart and an acutely inflamed bronchial tree with partially ulcerated mucosa. The lungs showed severe hemorrhagic edema. Analysis of the blood revealed an F concentration of 0.4 mg/100 ml (normal is about 4 μg/100 ml [30]).

The second worker [33] had all degrees of burns over 10% of his body surface and a small corneal ulcer in the right eye. He was acutely ill at the time of admission. He complained of nausea, numbness and tingling of hands and arms, and shortness of breath. He showed signs of bronchospasm and was cyanotic. High fever appeared within 2 hours. Urinalysis revealed 2+ albumin and numerous erythrocytes. He died 10 hours after the accident from cardiac arrest. Autopsy showed dilatation and local inflammatory changes of the heart, inflammation and partial ulceration of the larynx, trachea, and bronchial tree; extensive acute pneumonitis and pulmonary edema, and acute hyperemia in all other organs. The F content of the blood was 0.3 mg/100 ml.

Kleinfeld [34] in 1965 observed a case of acute pulmonary edema in a 29-year-old chemist who was exposed accidentally to HF when a vat containing HF acid broke. The acid spilled on the face and upper extremities, producing first- and second-degree burns. The workman developed pulmonary edema 3 hours after exposure and died 10 hours after admission to the hospital. At autopsy, severe tracheobronchitis and hemorrhagic pulmonary edema were found.

Machle et al [35] in 1934 reported the effects of airborne HF on two human subjects. The highest concentration that they were able to tolerate for more than one minute was 100 mg/cu m. At this level, there was smarting of the exposed skin in less than one minute, and conjunctival and respiratory irritation was marked. At 50 mg/cu m, the same effects were noticed with the exception of the skin irritation, but tickling and discomfort in the larger air passages were noticeable with each inspiration. At 26 mg/cu m, eye and nose irritation was mild and could be tolerated for several minutes. There was no cough or sneezing. The taste of HF was reported at all three concentrations.

Largent [26] in 1961 presented the results of experimental inhalation studies on five human subjects. They were exposed 6 hours/day, 5 days/week, for 10-50 days, at average concentrations of 1.42-4.74 ppm (1.16-3.89 mg/cu m) HF. Slight irritation of the nose was noticed in all subjects at concentrations averaging 2.59-4.74 ppm (2.12-3.89 mg/cu m) ranging from 1.8-7.9 ppm (1.5-6.5 mg/cu m). No signs or symptoms of lower respiratory tract irritation were reported at these average concentrations.

Elkins [36] reported complaints of nosebleeds in workers engaged in the HF etching process and in one plant where welders were exposed at 0.4-0.7 mg of "fluorine"/cu m. No other environmental data were provided.

(e) Effects in Bone

Wilkie [37] in 1940 described osteosclerotic bone changes in a 64-year-old worker who had been engaged in the preparation of HF for 16 years. It was noted that in addition to HF, he probably was exposed to fluorspar (CaF2) dust. Radiologic examination of the spine and pelvis showed very dense sclerosis and the forearms and lower legs revealed extensive ligamentous ossification. A 24-hour urine specimen showed a urinary F excretion of 15.22 mg/liter. The patient was completely free from any symptoms.

Largent et al [38] in 1951 found slight skeletal sclerosis in three workers exposed to HF. The ages of the workers were 46, 54, and 55 years, and lengths of service were 17, 14, and 10 years, respectively. The roentgenologic findings in one worker were described as a slight increase in the density of the lower thoracic spine, with calcification extending into the attachments of the lateral ligaments, together with some increased density in both ilia and in the sacrum. None of the workmen were disabled. Average urinary F concentrations for the three workers over a 3-year period were 12.29, 10.62, and 10.09 mg/liter, respectively. The urine samples were collected in 1-gallon jugs while the men were away from work. The period of collection covered several days, giving a reasonable representation of the average urinary F excretion for each period of collection. Additional cases of osteosclerosis in HF workers are presented in the epidemiologic studies. [39-41, HR Henderson, written communication, September 1974]

(f) Absorption and Excretion of F

In 1947, Largent [42] reported on the urinary F excretion of men employed in alkylation plants using the HF process. Urine was collected in 1-gallon glass containers during the hours when the men were not at work until 2-3 liters had been accumulated. Analysis of 502 samples received in the course of almost 3 years showed that only 1 sample had an F concentration greater than 4 mg/liter. The frequency distribution of F concentrations in the urine samples was as follows: 78% (393) were in the range of 0.1-0.9 mg F/liter; 18% (92) in the range of 1.0-1.9; 2% (11) in the range of 2.0-2.9; 1% (5) in the range 3.0-3.9; and 0.2% (1) in the range of 4.0 mg F/liter and above. It is probable that slightly higher urinary F concentrations would have been obtained if nonreactive (eg, wax-coated) containers had been used.

Collings et al [43] conducted a study to determine the absorption of inhaled HF. Two human subjects were exposed for an 8-hour period in an industrial environment to fluorides consisting primarily of HF and silicon tetrafluoride at an average airborne concentration of 3.8 mg F/cu m. Urine specimens were collected at 2-hour intervals during exposure and for approximately 2 days afterwards. There was a rapid rise in urinary F excretion during exposure, and a peak output was reached in 2-4 hours after cessation of exposure. Within 24 hours, the urinary F levels returned practically to base levels, although a slight elevation persisted into the following day. The total amounts of F excreted daily by the two subjects were as follows: day of exposure, 9.64 and 8.56 mg F; first day after exposure, 1.67 and 2.49; second day, 0.99 and 1.31; and third day, 0.89 and 1.34. The baseline daily urinary F excretions before exposure were 0.9 and 1.2 mg F, respectively.

For comparison, [43] the two subjects were then exposed to F at an average concentration of 5.0 mg F/cu m (in rock phosphate dust) "many weeks later," after the urinary F levels had been normal for "a long time." As with HF, there was a rapid rise in urinary F output during exposure, reaching a peak 2-4 hours after exposure and decreasing to base levels within 12-16 hours after exposure. The daily urinary F outputs of the two subjects were as follows: day of exposure, 10.0 and 9.95 mg F; first day after exposure, 1.96 and 2.99 mg F; second day, 1.28 and 1.10 mg F; and third day, 0.73 and 0.98 mg F. In proportion to the respective airborne F concentrations, the rapidity of absorption and the total amount of F excreted would indicate that HF and inorganic fluoride dust are equally well absorbed and excreted.

In a follow-up study, Collings et al [44] compared urinalyses of two subjects exposed for 6 hours to airborne fluorides (the relative proportions of gaseous and particulate F were not given) averaging 4.8 mg F/cu m in an industrial environment. One subject was considered to have had no previous F storage; the other subject had worked approximately 8 years in a plant having exposure to fluorides. An excretion curve plotted for the two subjects was remarkably similar for the first day following exposure; thereafter, for an additional and concluding period of slightly less than 3 days, the previously exposed worker maintained a consistently higher base F level than the subject with no previous F exposure. The authors suggested that the persistent high base level may have been due to a cumulative effect from repeated exposures. Urinary excretion values ranged from about 0.1 to 1.3 mg F/2 hours and were determined on the entire urine output during the study. An additional seven industrial workers exposed to airborne F concentrations from 2.5 mg F/cu m to over 10 mg F/cu m were found to excrete urinary F concentrations ranging from 5.3 to 23 mg F/liter (postshift). The values 48 hours later (preshift) were from 1.2 to 5.6 mg F/liter. Among eight other workers with exposures ranging from 0 to over 10 mg F/cu m, preshift urinary F concentrations ranged from 0.8 to 4.0 mg F/liter. The corresponding postshift samples ranged from 3.2 to 17.0 mg F/liter. [44]

Rye [45] in 1961 reported on urinary F excretion studies in two workers with no previous F exposure. They were exposed on five different occasions for an 8-hour shift to HF and silicon tetrafluoride gases at an average concentration of 2.4 ppm (1.9 mg/cu m) as F. The urinary F levels increased during the first 2 hours of exposure from a baseline value of 0.5 mg/liter, to 4.0 mg/liter, reached a peak of 7-8 mg/liter in the ensuing 10 hours, and returned to within the range of 0.5-1 mg/liter by the evening of the same day, or early morning of the next day. During the following 24-72 hours, without any additional exposure, the urinary F excretion rose at the same time of day as during exposure to a peak of 4-5 mg/liter, and only on the third day after exposure did it remain consistently at the preexposure level. The total urinary F excretion after the 8-hour exposure to gaseous F at 2.4 ppm was 4.5 mg on the day of exposure, and 3.8, 3.6, and 1.2 mg on the following days, respectively. These levels were similar to preexposure excretion of 1-1.4 mg/day.

In 1961, Largent [26] studied HF inhalation and F excretion in 5 human subjects exposed for 6 hours/day, 5 days/week, for up to 50 days at HF concentrations averaging 1.42-4.74 ppm (1.16-3.89 mg/cu m). For the purpose of studying the absorption and excretion of fluoride, the dietary intake of F by all five subjects was measured throughout the entire period of observation. No unexpectedly large variation in the uptake of dietary F was detected. There was a marked increase in fecal elimination of F from preinhalation levels of 0.062-0.195 mg F/day to 0.262-0.7 mg F/day during HF inhalation. Since there was no significant change of dietary F intake during exposure, compared with preexposure levels, the increase in fecal F excretion was reported to have been attributable only to the HF exposure.

The average daily amounts of F excreted and the average concentrations of F in urine samples collected during the experimental inhalation of HF are given in Table III-3.

Daily variations in the amount (mg F/sample) and in the concentrations (mg F/liter) in the urine of two subjects showed a rapid rise in urinary F excretion during exposure with a return to near preexposure levels on days when no HF was inhaled. Urinalysis before and after completion of the experiment did not reveal abnormal findings (EJ Largent, written communication, January 1975).

TABLE III-3

FLUORIDE ELIMINATION IN URINE IN RELATION TO THE INHALATION OF HF BY FIVE HUMAN SUBJECTS

Subjects	Number of Days	Average Concentration of Inhaled HF		Average Urinary F Values	
		ppm	mg/cu m	mg/liter	mg/day
E.L.	15	1.42	1.16	4.49	3.46
G.G.	25	2.59	2.12	9.47	9.33
K.W.	30	2.72	2.23	7.75	8.83
G.G.*	15	2.84	2.33	10.58	11.47
K.W.*	15	2.98	2.44	7.77	9.40
E.L.	10	3.39	2.78	7.30	6.69
G.B.	50	4.22	3.46	9.62	15.51
E.L. Jr.*	15	4.59	3.76	17.86	12.20
G.B.*	20	4.73	3.88	12.10	19.60
E.L. Jr.	25	4.74	3.89	15.86	10.77

*These values relate only to the final weeks of the inhalation periods of these four subjects.

From reference 26

Epidemiologic Studies

Machle and Evans [46] in 1940 published clinical findings from a group of workmen exposed principally to HF and, to a lesser degree, to calcium fluoride dust in a HF-acid manufacturing plant. At the beginning of the plant operation 9 years prior to the publication of this study, [46] mechanical difficulties caused frequent "severe" exposures. After installation of ventilation and controls, the air was ordinarily free from HF and fluoride dust. F was not detected in air samples taken in the center of the plant under normal operating conditions. Air samples taken in the neighborhood of equipment, or while repairs were being made, revealed 11-21 mg F/cu m. Periodic physical examinations including chest X-ray, hemoglobin, and red and white cell counts over a 5-year period did not show any significant findings. The mean urinary F excretion of exposed workers was 3.65 mg/liter. Of the 46 urine samples obtained over the 5 years (time of collection during day not given), 38 contained less than 4 mg F/liter; 4 contained 4-10 mg F/liter; and 4 had 16-24 mg F/liter. Roentgenologic examinations of the pelvis and spine of 10 men working with the greatest potential exposure did not show skeletal fluorosis after 5 years of intermittent exposure.

A study of a group of 74 men who had been exposed to HF for an average of 2.7 years was reported by Evans [47] in 1940. There had been many operating difficulties and the "fumes" had been so severe at times that windows and eyeglasses would etch in a short time. On a few occasions, there had been cases of upper respiratory tract irritation. Repeated chest X-rays over a 5-year period did not reveal any visible evidence of lung changes and did not differ from those of unexposed workers. Periodic clinical examinations and data procured for health insurance purposes did not show a higher incidence of pulmonary infection in the exposed workers. Their death rate from pneumonia and other pulmonary infections was the same as that of unexposed plant employees.

Peperkorn and Kahling [39] in 1944 studied clinical and radiologic findings in 47 employees who were exposed to HF-acid vapor and cryolite. Because of the working arrangement of the plant, a distinction between these two groups of workers could not be carried out. No environmental data were given, but on visual inspection extremely fine "fluoride" dust was found all over the plant. Nearly all of the workers complained of mild-to-moderate back pain and stiffness which in some cases included the cervical spine. Some complained of pain in the thighs. Knee complaints were often mentioned. The majority of the men reported shortness of breath on exertion. There was little evidence of cough, expectoration, or asthmatic conditions. With the exception of HF burn scars on various parts of the body and rigidity of the chest in many workers, physical findings were essentially normal. Red and white blood counts, hemoglobin, sedimentation rate, and urinalysis were all within normal values. Only one worker, age 44, who had worked for 15 years with sodium fluoride had evidence of mottled teeth. Relatively few carious teeth were observed.

On radiologic examination of the osseous system 34, or 72%, of the 47 workers showed osteosclerotic changes. [39] Of these, 14 had first-degree osteosclerosis; 11, second-degree; and 7, third-degree. Characteristics of first-degree osteosclerosis included increased bone density and thickened and misshapen structure of the trabeculae with the marginal contours of the bones exhibiting slight blurring. In second-degree osteosclerosis, these findings were more pronounced. The outer boundaries of the bones had become more irregular, insertions of the tendons had started to calcify, and the cortical substance of the long bones was widened, restricting the medullary canal. In third-degree osteosclerosis, the bone had become radiographically opaque and the insertions of tendons and ligaments and interosseous membranes were calcified.

In the previously described osteosclerotic changes, the first evidence of change was found in the pelvis and lumbar spine. As the process advanced, the changes spread to the rest of the spinal column and the ribs, with extremities affected last.

The degree of radiologic changes increased with the duration of employment. [39] Of the 47 workers examined, 40 were exposed during the whole work shift; of these, 8 with an average employment of 9 years ranging from 2 to 20 years had no osteosclerotic changes. Fourteen workers with first-degree changes had an average employment of 12 years, ranging from 3 to 17 years. Eleven workers with second-degree changes had an average of 18 years of employment, ranging from 7 to 27 years, and 7 workers with third-degree changes had an average employment of 22 years ranging from 15 to 32 years. Of the seven workers exposed only occasionally, five having an average of 21 years' exposure time ranging from 8 to 35 years had no osteosclerotic changes, while the remaining two workers had first-degree changes after 23 and 28 years of exposure, respectively. First-degree radiologic changes were observed no sooner than after 3 years of employment; second-degree changes, no sooner than after 7 years; and third-degree changes, no sooner than 15 years. Of the seven workers with third-degree changes, six were exclusively employed in the production of HF acid, whereas only one case originated in the cryolite shop. Although a higher prevalence of third-degree osteosclerosis was observed in HF-acid workers, first- and second-degree cases were apparently distributed at random among the different occupations. For most cases, the subjective complaints ran parallel to the severity of radiologic changes.

The case history of a 40-year-old worker who was employed for 15 years in the HF plant was presented by Peperkorn and Kahling [39] in 1944. After 7 years of employment, he began to have "rheumatic pains" which, over the years, increased until he became totally disabled. He complained of stiffness in all joints, except hands and feet. He had difficulty in breathing when walking or climbing. On physical examination, he was prematurely aged, emaciated, and pale. He had a stiff posture and walked with small steps. Chest expansion was limited, as were movements of the spine, hips, and shoulders. Red and white blood counts, sedimentation rate, blood calcium, and urinalysis were all reported normal. No urinary F levels were obtained. X-rays of the skeletal system showed third-degree osteosclerosis.

Dale and McCauley [40] in 1948 provided data on medical and dental conditions of 40 workers engaged in the production of HF acid for 2-33 years. Eleven unexposed office and warehouse workers served as controls. No workplace airborne HF levels were given, but it was reported that window glass in buildings housing the HF acid retorts corroded in a few months' time and had to be replaced periodically. Some of the workers in close proximity to the retorts experienced transitory hyperemia of the exposed skin. This was encountered more frequently during warm weather and in those workers who perspired excessively. The skin of the faces and hands appeared dehydrated, roughened, and irritated in the majority of the workers. Ulcers, chiefly on the hands and forearms, were observed in workers who had been splashed accidentally by HF acid. Dental examination showed fewer caries and fillings in the exposed group. Dental roentgenologic examinations revealed definite changes in the trabecular pattern of the osseous structure of the upper and lower jaws in 24 of the 40 workers and questionable changes in 8. The bone changes were characterized by an increase in the number and thickness of trabeculae and a corresponding decrease in the intratrabecular or canalicular spaces. Of the 32 with dental changes, marked bone changes were seen in 4 workers, moderate changes in 15, minimal changes in 5, and questionable changes in 8, with average years of exposure of 16.3, 14.7, 5.6, and 3.8 years, respectively.

The urinary fluoride excretion of 34 exposed workers which was determined by spot samples taken just before or just after working hours varied considerably, ranging from 0.89 to 49.3 mg/liter, with a mean of 10.8 mg/liter. [40] The distribution of urinary F was as follows: 4, 6, 10, and 14 workers had urinary F levels of 0.0-2.9, 3.0-5.9, 6.0-8.9, and over 9 mg/liter, respectively. On the basis of these single urine samples, there was no apparent correlation between urinary F excretion and the degree of bone changes found by dental roentgenologic examinations.

One of these workers, [40] aged 58, with an exposure history to HF and inorganic fluoride dust of 30 years, had been examined at the Cleveland Clinic. The results were reported in 1947 by McGarvey and Ernstene. [41] The workman felt well until 3 months before his visit to the clinic when he noted fatigue and dyspnea on exertion. The physical examination produced essentially negative results, except that the anterior-posterior diameter of the thorax was increased and the expansion of the chest was greatly limited. Urinalysis, red blood count, hemoglobin, white cell count and differential count, platelet count, bone marrow, blood serum calcium and phosphorus, and alkaline and acid phosphatases were all within normal limits. The roentgenogram of the skeletal system revealed marked radiopacity of the vertebrae, ribs, and pelvic bones with the bone structure almost completely obscured. The changes in the lower extremities were less advanced, and the bones of the upper extremities showed even less alteration. Relatively slight changes were present in the bones of the skull. A spot urine specimen taken 3 years earlier showed that this workman had been excreting F at a level of 23.1 mg/liter. [40] Alveolar bone changes noted in the mandible and maxilla at that time were described as moderate.

In 1961, Rye [45] reported the results of clinical observations, taken over a 3-year period, of workers engaged in the production of phosphoric acid. In this process, HF and silicon tetrafluoride were released, but engineering controls maintained the workplace airborne F concentrations below 3 ppm. Continuous air samples collected for one regular 8-hour shift showed an average exposure to be 2.4 ppm as "gaseous fluoride." Periodic medical and radiologic examinations of the chest revealed no abnormal findings. The author reported that no significant complaints of gastrointestinal or respiratory ailments were found in comparison with a control group consisting of an unspecified number of operational employees and clerical workers not exposed to HF. Urinary spot samples at the end of the shift were taken for each worker at least once every 3 weeks. Background urinary F levels were established by 5-10 determinations on each worker prior to his initial exposure. The author stated that no consistent urinary F excretion above 5 mg/liter was observed, but he gave no details.

The data obtained from studies of human exposures to HF alone are limited and insufficient to derive a standard which will prevent osteosclerosis. It therefore becomes necessary to make use of relevant studies which include reports on particulate or mixed particulate and gaseous inorganic fluoride exposures. The comparative absorption and excretion study of inhaled inorganic particulate fluorides and HF or silicon tetrafluoride by Collings et al [43] clearly indicates that the metabolism of F in humans is the same, independent of whether the F ion is inhaled as gaseous or as particulate inorganic fluorides. The absorption and excretion studies after inhalation of HF by Largent [26] and Rye [45] support the findings of Collings et al. [43] Based on the results of these investigations, relevant data obtained from any inorganic fluoride study can therefore be applied in establishing a standard for the prevention of osteosclerosis from HF exposure. The following inorganic fluoride studies are most relevant.

Derryberry et al [48] in 1963 reported the prevalence of osteosclerosis in 74 workers in a fertilizer-manufacturing plant in relation to fluoride exposure. Fluorides in the form of dust and gases in varying combinations and concentrations were produced throughout the process. Data were collected from clinical examinations, the working environment, and urinary F excretion throughout the 25 years of operation. Yearly, since 1952, a urine specimen was collected at the end of the shift on 5 consecutive days. An average daily (8-hour) exposure for each job was established by determining the time-weighted concentration of airborne F in the job environment. From these data, a weighted airborne exposure was calculated for the period of employment of each worker. Radiologic examination revealed a minimal, or questionable, increase in bone density in 17 (23%) of the 74 workers examined. The increased bone density was not associated with any musculoskeletal disability.

The range of individual TWA exposures to F was 0.50-8.32 mg/cu m, with 1.78-7.73 mg/cu m being associated with increased bone density or with a questionable increase in such density. [48] The difference in averages between the increased bone density group (average exposure: 3.38 mg F/cu m) and the remainder of the exposed group (average exposure: 2.62 mg F/cu m) was evaluated by NIOSH and found to be significant by both t test (one-tailed on logarithms of data, $t = 2.75$, $p = 0.0045$) and rank test ($Z = -2.2$, $p = 0.014$). Table III-4 shows the incidence of increased bone density as it relates to the level of time-weighted exposure during employment. It demonstrates that exposure to higher workplace airborne concentrations of F resulted in a relatively greater incidence of increased bone density.

Workers with a "high exposure," defined by Derryberry et al [48] as those with 50% or more of their postshift urine samples equaling or exceeding 4.0 mg F/liter, were likely to have increased bone density. Within the group of workers with increased bone density, 60.9% of the urine samples were 4.0 mg F/liter or greater in contrast with 47.5 % of the samples submitted by the group of workers without increased bone density. This difference is significant by both t test and rank test as performed by NIOSH (one-tailed analysis with $t = 2.44$, $p = 0.0095$ and $Z = -2.0$, $p =$

TABLE III-4

RELATIONSHIP OF WEIGHTED EXPOSURE DURING EMPLOYMENT TO INCIDENCE OF INCREASED BONE DENSITY IN 74 INORGANIC FLUORIDE WORKERS

Weighted exposure mg F/cu m	0-1.50	1.51-2.50	2.51-3.50	3.51-4.50	4.51-5.50	5.51-6.50	6.51-7.50	7.51-8.50
Number of workers	13	26	17	11	1	2	0	4
Number with increased bone density	0	5	6	4	0	1	0	1
Percent	0	19	35	36	0	50	0	25

From reference 48

0.036). The average excretion concentrations for the increased bone density group and the group without increase were 5.13 and 4.53 mg F/liter, respectively. Although the difference in average excretion concentrations is small, it is based on the averages of 38 urine specimens/man permitting a statistical evaluation suggesting that the difference is real ($t = 1.41$, $p = 0.085$ and rank test, $Z = -1.8$, $p = 0.023$). Table III-5 demonstrates that as the average urinary fluoride concentration increased there was a corresponding increase in the percentage of suspected osteosclerosis cases. Studies by the US Public Health Service [49] in 1967 evaluated the effects of chemical irritants on exposed workers in a chemical plant where HF was one of the primary chemicals produced. The two major sources of HF exposure were the firing kilns and process equipment leaks. Twenty-eight samples of airborne HF were taken with sampling periods ranging from 10 to 30 minutes. Results ranged from 0.07 to 10.0 ppm (0.06-8.2 mg/cu m), with a mean of 1.03 ppm (0.85 mg/cu m). Thirty-three samples for particulate F

TABLE III-5

RELATIONSHIP OF AVERAGE POSTSHIFT URINARY F CONCENTRATION TO INCIDENCE OF INCREASED BONE DENSITY IN 74 INORGANIC FLUORIDE WORKERS

Average urinary F excretion mg/liter	2-2.9	3-3.9	4-4.9	5-5.9	6-6.9	7-7.9	8-8.9	9-9.9	10+
Number of workers	10	23	20	9	3	1	5	2	1
Number with increased bone density	1	4	5	3	1	0	3	0	0
Percentage with increased bone density	10	17	25	33	33	0	60	0	0

From reference 48

were all under 0.5 mg/cu m, with a range of 0.1-0.49 mg/cu m. Pulmonary function tests were performed on 305 chemical workers including 11 workers exposed to HF, and a control group of 88 workers in a box plant. The mean of the chemical plant workers' ages was 44 years and these workers were, on the average, 14 years older than the box-plant workers. The observed values for Forced Vital Capacity (FVC), 1-second Forced Expiratory Volume (FEV 1), and FEV 1/FVC for the total group were within about 3% of the predicted normal with no significant difference between the chemical workers and the control group.

The residual volume (RV) expressed as percentage of total lung volume (TLVol) was 30.8% in the chemical workers, as contrasted with 26.8% for the box plant workers, with both values within normal limits (35% being the upper limit of normal). [49] As pointed out by the authors, the difference can be explained by the higher average age of the chemical workers, since

RV/TLVol usually increases with advancing years.

From the analysis of the pulmonary function data, the authors [49] concluded that ventilatory function in the chemical and box plant workers was, in most of the workers, within the acceptable age-adjusted normal limit. The decrease in function found in a small percentage of the workers appeared to be caused by smoking and not to be work-related.

Before-shift and after-shift urinary excretions were analyzed for F in 25 workers exposed to HF or particulate fluorides and in 10 nonexposed office employees. [49] Before-shift specimens were collected after the workmen had been away from the plant on their days off, and after-shift samples were collected after each consecutive workday for 5 days, and pooled for each man. The before-shift urinary F concentrations ranged from 0.33 to 4.48 mg/liter, compared to 0.95-26.6 mg/liter for the after-shift samples. Corresponding levels for the control group were 0.50-1.88 mg F/liter before the shift, and 0.50-2.38 mg F/liter for after-shift specimens. Of the 11 HF workers, 4 exceeded 5 mg F/liter (6.85, 8.80, 17.5, 26.6). The two workers with the highest urinary F levels had accidental exposures ("gas out" and reboiler leak) during the week of urine collection. Roentgenologic examinations of the lumbar spine of four HF workers with after-shift urinary F concentrations of 4.31, 6.85, 17.5, and 26.6 mg/liter did not show any skeletal fluorosis.

Additional follow-up data on environmental and urinary F levels on the same plant population have been provided by HR Henderson (written communication, September 1974). Data obtained between March 1968 and April 1973 using an automatic HF analyzer showed the following results: 2.1% of the total of 23,280 samples were 5 ppm (4.1 mg/cu m) and over; 1.3%, between 4 and 5 ppm (3.3-4.1 mg/cu m); 1.5%, between 3 and 4 ppm (2.5-3.3 mg/cu m); 3.2% between 2 and 3 ppm (1.6-2.5 mg/cu m); 11.4%, between 1 and 2 ppm (0.8-1.6 mg/cu m); and 80.3%, between 0 and 1 ppm (0-0.8 mg/cu m). Periodic urinary F samples taken for 6-10 years on 13 HF workers revealed that the average before-shift levels for the workmen ranged from 2.0 to 5.7 mg/liter, while average after-shift samples ranged from 4.2 to 24.7 mg/liter.

One of the four workers who earlier [49] had no X-ray evidence of osteosclerosis showed borderline or "first-degree" osteosclerosis on follow-up examinations 2 years later (HR Henderson, written communication, September 1974). There was no disability associated with the increased bone density. His average before-shift urinary F level was 5.3 mg/liter, ranging from 2.6 to 16.3 mg/liter, and average after-shift urinary F level was 11.5 mg/liter, ranging from 2.0 to 30.0 mg/liter. This worker had been employed for 11 years as a helper and kiln operator with HF exposure in the higher range of air concentrations sampled around the furnace.

In 1972, Kaltreider et al [50] reported the results of roentgenographic examinations and urinary F studies of potroom workers in two aluminum plants. In one plant, X-ray examinations of 79 potroom workers revealed increased bone density in 76. Forty-six workers (58.3%) were classified as having slight fluorosis, showing only accentuation of trabeculation and slight blurring of the bone structure; 4 (5.1%) had "moderate, diffuse structureless" bone appearance; and 26 (33%) were classified as having marked fluorosis. Limited motion of the dorsolumbar spine was found in 22 (20.6%) of the entire group of 107 potroom workers, compared to none in a control group (108 workers with no history of F exposure). The 8-hour time-weighted average F exposures of the potroom workers ranged from 2.4 to 6.0 mg F/cu m. The average urinary F concentration in spot samples taken during the day was 8.7 mg/liter for pot tenders, 9.8 mg/liter for tapper-carbon changers, and 9.6 mg/liter for cranemen. The average urinary F excretion for the controls was 0.7 mg F/liter. With the exception of a higher incidence (no data given) of aching joints, particularly those of the upper extremities in the exposed group, the medical history was not different in the two groups. Limited motion of the dorsolumbar spine was found in 22 (20.6%) of the potroom workers compared to none in the control group.

In the second plant, [50] roentgenographic examination of the spine showed no increased bone density in 231 potroom workers. No airborne F concentrations were given. Since the pots were hooded in this plant, the authors concluded that airborne F exposure was less than that in the other plant where electrolytic cells were not hooded.

In 1972, NIOSH conducted a study of an aluminum reduction facility for the primary purpose of collecting and analyzing airborne dust, coal tar pitch volatiles, fluorides, carbon monoxide and sulfur dioxide. [51] In addition, a limited amount of medical information was provided by the plant medical department. Of about 200 potroom workers receiving annual pulmonary function testing, 10 individuals with known or suspected respiratory problems were selected for more detailed tests consisting of chest X-rays, spirometry, and steady-state CO diffusion studies. Eight individuals (presumably all members of the selected group) were reported to have a respiratory problem prior to employment or a strong family history of asthma. Neither smoking histories nor actual results of respiratory tests were reported, but 7 of the 10 workers were stated to have marked-to-severe obstructive airway changes as evidenced by a reduction of FEV 1 and maximum breathing capacities. Although the age distribution was not provided, the examining physician expressed concern about "the young age distribution of the workers"; one of the workers was 39, and three workers were in their early forties. In addition, the results of urinary F analyses covering a 1-year period and involving about 155 workers (including potroom and cryolite workers) were made available. The average of the preshift samples was 2.35 with a range of 2.0-2.8 mg F/liter. The average of the postshift samples was 4.8, ranging from 3.2 to 6.5 mg F/liter. Results of breathing-zone and general air samples for gaseous and particulate F in the potroom over a 5-day period were all less than 0.094 mg F/cu m. Breathing-zone and general air samples taken during the same time period in the cryolite area were all less than 0.34 mg F/cu m (gaseous and particulate F). Because there was a previous history of respiratory disorder in most of those exhibiting obstructive airway changes, and fluoride was but one of several contaminants present in the potroom area, it is not reasonable to conclude that obstructive airway changes developed as a direct result of exposure to gaseous and particulate fluorides.

Animal Toxicity

Inhalation studies involving animals exposed to HF at concentrations ranging from 3 to 660 ppm (2.5-540 mg/cu m) were reported by Ronzani [52] in 1909. Five guinea pigs and five rabbits died in 0.5 and 1.5 hours, respectively, while being exposed to HF at an airborne concentration of 660 ppm (540 mg/cu m). When five guinea pigs and five rabbits were exposed to HF at 250 ppm (205 mg/cu m), they died in 1.0 and 3.0 hours, respectively. All animals showed severe signs of irritation from the start of the experiment, with increasingly labored breathing. Autopsy showed ulcerations of the upper respiratory tract and of the cornea of the eyes. The lungs were hyperemic and edematous. At 50 ppm (40 mg/cu m), five guinea pigs died in 2 hours, whereas the five rabbits displayed severe signs of physical distress after 3 hours. At a concentration of 30 ppm (25 mg/cu m), guinea pigs died after one day, while rabbits, exposed to HF at the same concentration, were in such poor condition after 3 days of exposure that the experiment had to be discontinued. Continuous exposure at 10 ppm (8 mg/cu m) for 5 days was not fatal to either species. In addition to labored breathing, the guinea pigs showed only slight irritation of the eyes.

Fifteen rabbits, 21 guinea pigs, and 4 pigeons were then exposed to HF at 10 ppm (8 mg/cu m) for two 3-hour periods/day for 31 days. During these periods, two rabbits, seven guinea pigs, and one pigeon died. At autopsy, opacity of the corneas with ulcerations, lesions of the nasal mucous membranes, emphysematous lungs, bronchopneumonitis, and interstitial pneumonitis were found. The autopsy of one of the rabbits surviving the exposure periods showed similar, but less severe, pathologic findings. All surviving animals had lost up to 23% of their original weight and had severe anemia. After immunization against typhus, four surviving rabbits were considerably less efficient in producing agglutinizing substances than were controls; after immunization five experimental guinea pigs showed a marked decrease in production of specific antibodies. Exposed guinea pigs had reduced resistance to bacterial infection in the lungs. While experimental animals were less resistant than controls to the effects of inoculation with diplococcus and tuberculous bacilli, the opposite was true in the case of anthrax.

Further experiments [52] using HF concentrations of 7.5, 5, and 3 ppm (6, 4, and 2.5 mg/cu m) established 3 ppm (2.5 mg/cu m) as a no-effect concentration. A 30-day exposure of 16 rabbits, 20 guinea pigs, and 3 pigeons to HF at 3 ppm (2.5 mg/cu m) did not produce any pathologic changes.

Machle et al [35] in 1934 reported on acute effects in rabbits and guinea pigs exposed to HF at concentrations of 24-8,000 mg/cu m for periods ranging from 41 hours to 5 minutes. Three rabbits and three guinea pigs were used for each exposure. Evidence of eye and respiratory tract irritation was noticeable in all animals at all concentrations, although for those animals exposed at 50 and 24 mg/cu m for 5-15 minutes, signs were mild and not immediate. Slowing of the respiratory rate was uniform and particularly noticeable in rabbits. Paroxysmal coughing and sneezing occurred more frequently as the airborne HF concentration was increased. One rabbit exposed 6 hours/day for a total of 41 hours at 24.5 mg HF/cu m suffered considerable liver and kidney damage. Weakness and the appearance of illness were prominent in all animals exposed at more than 500 mg/cu m for 15 minutes or longer. Signs became increasingly severe as the airborne HF concentration was increased. Animals exposed at concentrations of 3,000 mg/cu m or more for 5-15 minutes exhibited edema or cloudy swelling of organs and tissues. No deaths occurred at concentrations of 1,000 mg/cu m for up to 30 minutes of exposure, at 100 mg/cu m for 5 hours, or at 24 mg/cu m for 41 hours. Rabbits which survived returned to normal appearance and activity in a few days to a few weeks, while guinea pigs showed a definite tendency to delayed response and death between the fifth and tenth week following exposure. The predominant lesions found in exposed animals were pulmonary hemorrhage, congestion, emphysema, and edema, with secondary infection in many instances; hepatic congestion with evidence of parenchymal necrosis and fatty degeneration; splenic congestion and edema; renal congestion, edema and tubular necrosis; and myocardial congestion, edema, and necrosis. Corneal erosions and ulcerations of nasal turbinates were observed in numerous animals exposed to "higher" concentrations. A number of these changes were also common to control groups, and were therefore considered as normal occurrences. The authors were unable to determine to what extent these changes were due to spontaneous disease processes, infection, nutritional causes, or to possible dietary deficiencies.

In 1935, Machle and Scott [53] studied the distribution of F in the tissues of animals exposed to airborne HF at different concentrations and exposure times (expressed in milligram-hours). Six rabbits were used as controls. The exposed animals were divided into two groups. Group 1 consisted of four rabbits with an exposure of 1 mg-hour or less; three were exposed to HF at 53 mg/cu m, and one to HF at 24 mg/cu m. Group 2 consisted of four rabbits, one guinea pig, and one monkey, with an exposure of 4.56 mg-hours; all were exposed to HF at 15.2 mg/cu m. The interval between exposure and autopsy ranged from 9 to 14 months. The results indicated that abnormal amounts of F were held in tissues, chiefly in bones, for as long as 14 months following exposure.

Machle and Kitzmiller [54] in 1935 reported the effects of airborne HF on five rabbits, three guinea pigs, and two Rhesus monkeys exposed at a concentration of 15.2 mg/cu m for 6-8 hours daily except on weekends until a total of 309 hours of exposure had accumulated. Eight rabbits, five guinea pigs, and one monkey were used as controls. Except for two guinea pigs, all animals survived 8 months after conclusion of the exposure; all except one monkey were then killed and necropsied. There was no pronounced response following introduction of the animals into the exposure chamber. Occasional coughing was noted only in one monkey during the first week of exposure. Slight lacrimation was exhibited by all the animals. Erythrocyte counts of the exposed rabbits were significantly lower than those of controls. No evidence of injury to the corneas or nasal passages was observed. Significant pathologic findings were limited to the lungs, liver, and kidneys and were marked in the two guinea pigs that died during the study. One guinea pig that died after 160 hours of exposure showed a large pulmonary hemorrhage. The bronchial epithelium was thickened and sloughed off in many areas. The liver was moderately congested and showed advanced fatty degeneration. The other guinea pig that died after 134 hours of exposure showed a low-grade inflammatory reaction in the alveolar walls with atelectasis, and marked degenerative changes and hyperplasia of the bronchial epithelium. The liver showed scattered necrosis, some changes in fatty tissue, and diffuse periportal fibrosis. The kidneys had spotty tubular necrosis. The guinea pig that survived showed pulmonary hemorrhages, alveolar exudates, and cellular infiltration of the alveolar wall with irregular thickening. The liver showed considerable lobular degeneration and necrosis. The lungs of all rabbits revealed leukocytic infiltration of the alveolar walls with or without edema or thickening, and secondary infection was evident in two animals. Marked degeneration of fatty tissue was seen in the livers of two rabbits. Extensive renal tubular degeneration and necrosis associated with fibrous tissue replacement were found in all exposed rabbits. Glomerular changes consisted of inflammation and degeneration. Except for the kidneys, which showed long-standing degenerative and inflammatory changes, the organs of the monkeys showed scarcely any lesions attributable to exposure.

Stokinger [55] in 1949 reported the exposure of 29 rats, 20 mice, 20 guinea pigs, 18 rabbits, and 4 dogs to gaseous HF at 25 mg HF/cu m and 7 mg HF/cu m for 6 hours/day, 6 days/week for 5 weeks. A second group of 15 rats, 20 mice, 10 guinea pigs, 10 rabbits, and 5 dogs was exposed at 7 mg HF/cu m for the same period. Subcutaneous hemorrhages, particularly noticeable around the eyes and on the feet, developed in rats within a few days. Mice were similarly affected, but to a lesser degree. In dogs, an inflammation of the scrotal epithelium became apparent after the third day of exposure. These findings were confined mainly to the group exposed at the 25 mg HF/cu m level, but hemorrhagic areas, less severe in nature, did develop on the feet of rats at the 7 mg/cu m level. Death occurred only at 25 mg HF/cu m and exclusively in rats and mice which had a mortality rate of 100%. Deaths occurred in rats throughout the entire exposure period, while all mice died by the seventieth hour of exposure. At the 25 mg HF/cu m level, rats showed pronounced loss in weight; rabbits, only a slight loss; dogs, no change; and guinea pigs, after a consistent gain, a loss in weight following the third week of exposure. Approximately normal weight gains were observed in all animals at the 7 mg HF/cu m level.

Determinations of blood calcium, alkaline phosphatase, and serum protein in dogs and rabbits showed no changes of significance at either level. Overnight urinary F excretion of rabbits exposed at the 7 mg HF/cu m level increased 5-fold over control values. There was a significant increase in blood fibrinogen level in dogs and rabbits exposed to HF at 25 mg/cu m, while the prothrombin time remained normal.

At autopsy, 27 out of 44 animals examined showed hemorrhages and edema of the lungs. [55] Degenerative testicular changes and ulceration of the scrotum were found in four dogs. In rats, renal cortical degeneration and necrosis were noted in 27 of 30 animals. The above pathologic changes were found only at the 25 mg HF/cu m level. At the 7 mg HF/cu m level, localized hemorrhagic areas in the lungs were noticed only in one out of five dogs. Serial determinations of fluoride concentration in bone of animals exposed to HF from 25 to 95 hours at 25 mg/cu m showed a progressive increase of fluoride. The F content of the teeth of rats increased as much as 300%. Somewhat smaller increases were found in the femur. Increases in the F content of the maxillary and mandibular bones of dogs ranged from 200 to 300%. The F content of bones of animals exposed to HF at 7 mg/cu m for 166 hours was, on the average, somewhat lower than that found at the higher level. At almost equal Ct (concentration x time) values of 1200 and 1162 (25 mg HF/cu m for 50 hours and 7 mg HF/cu m for 166 hours, respectively), F deposition was approximately the same.

Blood F levels following exposure to HF were determined by Smith and Gardner [56] in 1949. Ten rabbits were exposed 6 hours/ day for 1-5 days to HF at a concentration of approximately 29 mg/cu m. Two rabbits served as controls. Blood specimens, obtained by heart puncture, were taken from two animals after each exposure day. Postexposure samples were obtained at intervals up to 6 days after termination of exposure. Blood F levels determined immediately after exposure to HF ranged from 35 to 122 μg/100 ml blood, as compared to 9-15 μg/100 ml in the two control animals. The blood F level reached a plateau during the first day of exposure and did not significantly increase in spite of continued exposure. Lower, but still abnormally high, blood F levels (15-48 μg/100 ml) persisted for at least 3 days after cessation of exposure. Normal values were reached 6 days after exposure. The only outward evidence of an adverse effect was irritation of the eyes.

Stokinger et al [57] in 1950 reported the effects of airborne HF on 20 rats exposed 6 hours/day, 5 days/week at an average concentration of 8.0 mg HF/cu m for a total of 124 hours. A second group of 10 rats was exposed on alternate days to the same concentration for a total of 62 hours. One animal in the second group died, but the cause of death appeared to be infection and not the exposure. The weights of the animals never went below preexposure values; in fact, a progressive weight increase occurred during exposure. Microscopic examinations revealed no lesions attributable to the exposure to HF. The F content of teeth and bones in the first group of animals was 1.5-1.8 times the F content of similar teeth and bones in the second group.

In 1955, Klauder et al [24] described the irritant action caused by application of various concentrations of HF acid on the skin of rabbits. Hydrogen fluoride at concentrations of 1-50% was placed separately on the inferior dorsal aspect of the shaved ear, allowed to remain for 5 minutes, then rinsed in running water for 15 minutes. No reaction resulted from applications of 1-4% HF acid. Transitory blanching occurred from applications of 6-10% HF acid. After applications of 12-22%, crust formation appeared in about 24 hours at the site of the blanching and disappeared in about one week. Applications of 25% and 30% HF acid caused blanching, followed by redness and, later, by crust formation. These effects, along with blisters and superficial ulceration, were observed at 35% and 40%. The reactions were more pronounced when the HF acid concentration was raised to 50% and were followed by deep ulcerations. In the study employing higher concentrations, acid solutions were applied to both ears of some animals, after which one ear was rinsed with water and the other was not. The reaction on the unrinsed ear was more pronounced than that of the rinsed one, substantiating the importance of immediately rinsing the site of HF acid contact.

Rosenholtz et al [58] in 1963 reported on brief single exposure effects in animals. Rats were exposed in groups of 10 to HF in various concentrations for single 5, 15, 30, and 60-minute periods. The calculated LC50 values for rats were 4,060, 2,200, 1,670, and 1,070 mg/cu m, respectively. The LC50 for 10 guinea pigs exposed for 15 minutes was 3,540 mg/cu m. All animals showed signs of respiratory distress and conjunctival and nasal irritation. Pathologic studies revealed nasal passage necroses, renal tubular damage, hepatocellular congestion and inflammation, and acute inflammation of the skin. No pathologic changes of the lower respiratory tract were reported.

The acute toxicity of short 5-minute exposures to HF was reported by Higgins et al [59] in 1972. Ten rats and 15 mice in each group were exposed to HF in a series of concentrations to determine LC50 values. The animals were observed for 7 days following exposure in order to include any delayed deaths due to pulmonary edema. The 5-minute LC50 for rats was 18,200 ppm (14,900 mg/cu m) and for mice it was 6247 ppm (5120 mg/cu m).

The response of enzyme systems in the skin of the guinea pig to the toxic action of the fluoride ion was investigated by Carney et al [60] for the purpose of evaluating the effectiveness of various agents commonly used for first-aid treatment of HF and HF-acid burns. The experimental system used consisted of freshly excised guinea pig ear skin incubated at 37 C on a special growth medium to which various amounts of HF acid or sodium fluoride were added. First-aid treatments were simulated by adding fluoride-binding compounds to the medium or by transferring the skin to a fresh fluoride-free medium. The responses measured were: the inhibition of enolase activity, skin respiration (oxygen uptake), and tetrazolium reductase activity. The results indicated that transferring the skin to a fresh medium to simulate washing was an effective method of counteracting the toxicity of the fluoride ion. It was pointed out by the authors, however, that washing can remove fluoride from the surface of the skin, but if calcium compounds (F binding agents) are injected into the tissues to inactivate F ions, the compound calcium fluoride is formed which remains in place. Two calcium compounds, calcium chloride and calcium gluconate, were found to be nontoxic to skin in the laboratory and were both effective in counteracting the fluoride ion. Magnesium was less effective than calcium chloride and benzathonium chloride did not produce a significant effect. Lanthanum chloride effectively removed fluoride but had an adverse effect upon the respiration and viability of skin cells.

In summary, animal studies indicate the primary toxic effect of HF to be on the respiratory system [35,52,54,55] with pathologic tissue changes also found in the kidneys [55,58] and liver. [54,58] Short exposures of up to 3 hours to HF at concentrations of 200-20,000 mg/cu m resulted in severe irritation of the respiratory tracts and eyes of rabbits, dogs, guinea pigs, rats, and mice, followed by death in the majority of the exposed animals. [35,52,58,59] The results of prolonged exposure to airborne HF at concentrations more relevant to determining a safe exposure limit were reported in three studies. [52,54,55] Rats, mice, guinea pigs, rabbits, and dogs exposed to HF at a concentration of 25 mg HF/cu m for 6 hours/day 6 days/week for 5 weeks [55] showed moderate pulmonary edema and pulmonary hemorrhage. Renal degeneration and renal necrosis were found in rats. Pulmonary, renal, and hepatic tissue damage in various degrees in rabbits, guinea pigs, and monkeys occurred at a lower concentration (15 mg HF/cu m) but in a similar exposure period. [54] Localized hemorrhagic areas in the lungs were noticed in one out of five dogs at 7 mg/cu m, [55] while inflammatory respiratory changes and a mortality of 10/40 in rabbits, guinea pigs, and doves were reported at about the same exposure level and period in another experiment. [52] When exposed to airborne HF at 2.5 mg/cu m, 6 hours/ day for 31 days, rabbits, guinea pigs, and doves experienced no adverse effects. [52] Corneal ulcerations were observed in all animals at concentrations as low as 8 mg HF/cu m. [52]

The most significant findings of the animal studies, besides the effect on the respiratory system, were renal tissue damage [55,58] and hepatic [54,58] tissue damage. These effects occurred as the result of exposures to HF at concentrations as low as 15 mg/cu m. [54]

Several animal studies [53,55,57] have shown that inhalation of HF resulted in increased deposition of F in osseous tissue. The F content of various bone structures following exposure to HF at 25 mg/cu m increased progressively as much as 300% as exposure time was extended from 25 to 95 hours. At the 7 mg HF/cu m exposure level, the F content of these bone structures was somewhat lower. [55]

The destructive action of the F ion on enzyme systems in the skin of the guinea pig was counteracted by the use of calcium, magnesium, and lanthanum compounds. [60] Calcium proved to be more effective than either magnesium or lanthanum. In addition, the use of lanthanum had an adverse side effect.

Table XII-3 summarizes the above mentioned animal exposure-effect data.

Correlation of Exposure and Effect

(a) Acute Irritating Effects

Two workers splashed with HF and thus exposed to airborne HF at a concentration estimated by the authors to be between 10,000 and 100,000 ppm (8,200-82,000 mg/cu m) for a few minutes died from pulmonary edema 2 hours following the initial exposure. [32]

During a short exposure to airborne HF at 100 mg/cu m, smarting of the skin and marked eye and respiratory irritation were observed. [35] This was the highest concentration that could be tolerated for more than one minute. At 50 mg HF/cu m, the same effects were noticed with the exception that the skin irritation was no longer experienced. At 26 mg HF/cu m, eye and nose irritation was mild but could be tolerated for several minutes.

Humans experimentally exposed to HF at concentrations which averaged 2.59-4.74 ppm (2.12-3.89 mg/cu m) and ranged from 1.8 to 7.9 ppm (1.5-6.5 mg/cu m) for up to 50 days developed mild irritation of the skin, eyes, and nose. [26] No signs or symptoms of lower respiratory tract irritation were reported at these airborne concentrations of HF. Exposure at an average concentration of 1.49 ppm (1.2 mg/cu m) ranging from 0.9 to 2.0 ppm (0.7-1.6 mg/cu m) did not result in any adverse effect.

(b) Effects of Chronic Exposure on the Respiratory System

Only one of the above studies [49] evaluated the respiratory effects of chronic exposure to HF. Ventilatory pulmonary function tests were performed on 305 chemical workers including 11 workers exposed to HF. Results of determinations of F in samples of air taken during the study ranged from 0.07 to 10.0 ppm HF (0.06-8.2 mg/cu m) with a mean of 1.03 ppm (0.85 mg/cu m). The observed values for FVC, FEV 1, and RV showed no significant difference between chemical workers and a control group.

Another study [45] did not reveal a higher incidence of respiratory complaints or abnormal chest X-rays in workers engaged in the production of phosphoric acid when compared to a control group. Air concentrations of HF and silicon tetrafluoride emitted during the process were kept, according to the author, below 3 ppm (2.5 mg/cu m), measured as HF. Results of air sampling were not reported except for one 8-hour exposure to gaseous fluoride which was 2.4 ppm (2.0 mg/cu m).

In a study of an aluminum reduction facility, 10 potroom workers with known or suspected respiratory problems were selected for further study out of 200 workers receiving annual pulmonary function testing. [51] Seven of the 10 were found to have marked-to-severe obstructive airway changes.

Determinations of airborne HF in the potroom made during a 5-day period were all less than 0.094 mg F/cu m. [51]

One human subject exposed to HF for 6 hours/day for 15 days at an average concentration of 1.42 ppm (1.16 mg/cu m) and exposed for 10 days at 3.39 ppm (2.78 mg/cu m) did not have abnormal pulmonary function 3 years after the experiment (EJ Largent, written communication, January 1975). One animal study [54] reported "significant pathological findings" in the lungs of five rabbits and three guinea pigs exposed to HF at 15.2 mg/cu m for 6-8 hours daily, except weekends, until 309 hours of exposure had accumulated.

(c) Effects on Kidneys

Animal studies [54,55] indicated renal tissue damage resulting from prolonged exposure to HF. The lowest airborne concentration of HF at which renal degeneration and necrosis occurred was 15.2 mg/cu m with a total exposure time of 309 hours. [54]

Serial urinalyses were performed on five human subjects (EJ Largent, written communication, January 1975) exposed in six separate experiments for 6 hours/day, 5 days/week up to 50 days to HF at six different concentrations, the averages of which ranged from 1.42 to 4.74 ppm (1.16-3.89 mg/cu m); the urinalyses did not show any abnormal findings.

(d) Effects on the Skeletal System

Several studies have reported osteosclerosis [37-39] and one study [40] has reported changes in the trabecular pattern of the osseous structure of the upper and lower jaws. However, data on airborne HF exposure were not given, making a correlation impossible. Changes in the skeletal system were found first in the pelvis and the lumbar vertebrae

[39] or were more easily discernible in those regions. [37,38] Dale and McCauley [40] recommended periodic X-ray examination of the jaws during routine examinations for fluorosis in workers exposed to chemicals. One study [46] found no evidence of skeletal fluorosis in 10 workers occasionally exposed to HF at 11-21 mg/cu m during repairs of leaking equipment. In another study, [49] four HF workers, selected for radiologic examinations of the spine because of their high postshift urinary F concentration, showed no changes in bone density at the time of the study. One of these workers showed "first-degree" osteosclerosis on a follow-up examination 2 years later (HR Henderson, written communication, September 1974). The average exposure to HF in the work area was 1.03 ppm (0.85 mg/cu m) ranging from 0.07 to 10.0 ppm (0.06-8.2 mg/cu m). The worker with osteosclerosis was a kiln operator and was exposed to HF at the higher range of concentrations found around the furnace.

The absence of environmental data in HF studies on osteofluorosis, as discussed in the section Epidemiologic Studies, makes it necessary to utilize data obtained from inorganic fluoride studies. Comparative inhalation studies of HF and inorganic fluorides [43] showed no difference in the metabolism of F.

The most comprehensive inorganic fluoride study which correlated environmental data and radiologic findings with changes in the osseous system provides sufficient data to establish a threshold for osteofluorosis. [48] From numerous determinations of F in air made over a period of many years, an 8-hour time-weighted average exposure was calculated for the period of employment of each worker. Results ranged from 0.50 to 8.32 mg F/cu m with an average of 2.81 mg F/cu m. Increased bone density or a questionable increase in such was found in 17 of the 74 workers examined. The average exposure experienced by these 17 workers was 3.38 mg F/cu m, ranging from 1.78 to 7.73 mg F/cu m. The difference in averages between the increased bone density group (3.38 mg F/cu m) and the remainder of the exposed group (2.62 mg F/cu m) was statistically significant. Also, exposure to HF at higher airborne concentrations resulted in a relatively greater incidence of increased bone density.

In an aluminum plant study, [50] 76 osteofluorosis cases in a group of 79 potroom workers were found; 46 were classified as minimal, 4 as moderate, and 26 as marked osteofluorosis. Restrictive motion of the spine was reported in 22 workers with osteofluorosis. Moderate and marked osteofluorosis were observed only after 15 or more years of employment. Workroom levels ranged from 2.4 to 6.0 mg F/cu m.

(e) Absorption and Excretion of F

Several studies [26,43,45] have evaluated urinary F excretion during and shortly after exposure. They showed a rapid rise in urinary F excretion during the first few hours of exposure, reaching a peak 2-4 hours after exposure and returning to near normal by the next day.

In six HF workers with osteosclerosis, urinary F excretion data were reported. Three workers with markedly increased bone density had urinary F concentrations of 23.1 mg/liter (spot sample), [40] 15.22 mg/liter (24-hour sample), and 1.73 mg/liter (24-hour sample). [37] Three workers with minimal bone changes had urinary F levels of 9.3-12.3 mg/liter in samples collected after work. [38] In 25 workers exposed to HF and particulate fluorides in a chemical plant, preshift urinary F concentrations ranged from 0.33 to 4.48 mg/liter compared to 0.95-26.6 mg/liter for the postshift samples. [49] A limited number of determinations of airborne HF (26) averaged 0.85 mg/cu m. Thirty-eight determinations of airborne particulate F were all under 0.5 mg/cu m. One worker with first-degree osteosclerosis had an average preshift urinary F level of 5.3 mg/liter, ranging from 2.6 to 16.3 mg/liter and an average postshift excretion of 11.5 mg/liter, ranging from 2.0 to 30.0 mg/liter (HR Henderson, written communication, September 1974). In the same communication, Henderson related that periodic urinary F levels over a 10-year period of 13 HF workers averaged from 2.0 to 5.7 mg F/liter (preshift) and 4.2-24.7 mg F/liter (postshift). Definite and questionable trabecular changes of the upper and lower jaws in 32 of 40 HF workers were associated with an average urinary F level (spot samples) of 10.8 mg/liter, ranging from 0.89 to 49.3 mg/liter. [40] Workers with moderate to marked changes had an average exposure of 15.1 years, while for minimal or questionable changes, the exposure period was 6.0 years.

In order to compare urinary excretion of an industrial worker presumed to have stored fluoride in the skeletal system with the excretion from a subject without stored F, two subjects were exposed to airborne fluorides averaging 4.8 mg F/cu m for 6 hours; subsequent excretion curves for the two subjects were very similar for the first day, but thereafter the previously exposed worker maintained a consistently higher base level than the subject with no previous F exposure. [44] Urinary concentrations ranged from about 0.1 to 1.3 mg F/2 hours. [44]

More comprehensive urinary F excretion data [48,50,51] have been provided in inorganic fluoride studies. In a fertilizer-manufacturing plant, [48] 17 of 74 workers with a minimal or a questionable increase in bone density had an average postshift (average of 38 specimens/man) urinary F excretion of 5.18 mg/liter, ranging from 2.8 to 8.9 mg/liter. The other 57 workers with no bone changes excreted an average of 4.53 mg F/liter, ranging from 2.1 to 14.7 mg F/liter. As the average urinary F excretion increased, the percentage of suspected osteofluorosis increased within each excretion range.

In 1 aluminum plant, [50] 76 of 79 potroom workers developed osteofluorosis. Average urinary F concentrations as determined by spot samples taken during the work shift ranged from 8.7 mg/liter for pot tenders to 9.8 mg/liter for tapper-carbon changers. Postshift samples would probably have shown higher values since urinary F excretion reaches a maximum 2-4 hours after exposure. [26,43,45]

In a second aluminum plant, [50] the average urinary F excretion (postshift samples) of 231 potroom workers with no increased bone density ranged from 3.0 to 10.4 mg/liter over a 5-year period; improved control measures and hygienic practices probably helped prevent high urinary F levels in this group. The average preshift F excretion after 48 hours off work was reduced from 3.6 to 1.4 mg F/liter when control measures were put into effect.

Urinary F analyses covering a 1-year period and involving about 155 aluminum workers (potroom and cryolite workers) were performed on both pre- and postshift samples. The average of the determinations of F in the preshift samples was 2.35 mg/liter with a range of 2.0-2.8 mg F/liter. The average of the postshift samples was 4.8 mg F/liter, ranging from 3.2 to 6.5 mg F/liter. [51] Results of analyses of breathing-zone and general room-air samples over a 5-day period were all less than 0.34 mg F/cu m (gaseous and particulate F). [51]

Table XII-4 summarizes the above mentioned human exposure-effect data.

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 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 (±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]

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 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

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 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 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 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.

V. DEVELOPMENT OF STANDARD

Basis for Previous Standards

Bowditch et al [163] reported in 1940 that Massachusetts was suggesting a 3 ppm (2.5 mg/cu m) MAC for hydrogen fluoride as a guide for occupational exposure.

In 1945, Cook [164] compiled a list of standards and recommendations for MAC's for industrial atmospheric contaminants. Three ppm (reported by Cook as equivalent to 2.0 mg/cu m, but actually equivalent to about 2.5 mg/cu m) was the value suggested for HF by California, Connecticut, New York, Oregon, Utah, and the US Public Health Service, while Massachusetts proposed 1.5 ppm (1.2 mg/cu m). There was no discussion of the MAC value in Massachusetts of 1.5 ppm (1.2 mg/cu m) which differed from the 3 ppm (2.5 mg/cu m) reported by Bowditch. [163] Cook reported a generally accepted MAC value of 3 ppm (2.5 mg/cu m).

The efforts of a committee within the American Conference of Governmental Industrial Hygienists (ACGIH) to develop a MAC which could be adopted by all the states was reviewed by Bloomfield [165] in 1947. The committee had received replies from 24 states and 3 cities. Three respondents did not list a MAC value for HF while 24 reported an established MAC value of 3 ppm (2.5 mg/cu m) for "fluorine (hydrogen fluoride)."

At its 1947 meeting, the ACGIH [166] accepted a MAC of 3 ppm (2.5 mg/cu m) for HF. It was not specified if this MAC was intended as a ceiling value or as a TWA. At its meeting in April 1948, the ACGIH [167] adopted a TLV of 3 ppm (2.5 mg/cu m).

Data presented in the 1962 Documentation of the Threshold Limit Values for Substances in Workroom Air [168] supported a 3 ppm or approximately 2 mg/cu m (sic) threshold limit for HF. However, the data referred to in the Documentation were primarily concerned with human exposure to fluoride and animal exposure to HF. One unpublished industrial medical study on workers exposed to 50% gaseous and 50% particulate fluorides was cited [168] which indicated that workers excreting urinary F values of 1.5-2.5 mg/day, corresponding to 1-4 ppm F in the working environment, would not be expected to experience any changes "of health significance." Elkins [36], however, stated that workers in the etching process had nosebleeds as did welders exposed to 0.4-0.7 mg F/cu m who were excreting 2-6 mg F/liter of urine but he did not cite any supportive environmental data. Other workers exposed to 0.1-0.35 mg F/cu m and excreting, on the average, 4.5 mg F/liter of urine reportedly experienced sinus trouble. [36] The ACGIH [168] suggested that the urinary excretion values reported by Elkins [36] seemed "inconsistently" high relative to airborne HF levels, and dietary F was suggested as a possible factor.

The 1966 Documentation [169] reiterated that the 3 ppm threshold limit for hydrogen fluoride was "securely based for protection against long-term chronic effects." References previously cited in the 1962 Documentation [168] formed the basis for the selection of 3 ppm. In order to take into account Elkins' [36] findings, this TLV was designated a ceiling limit in the 1966 Documentation. However, this ceiling limit was never proposed in any subsequent Threshold Limit Values booklet, including the 1971 Documentation, [170] published by the ACGIH.

The 1971 Documentation [170] again recommended a TLV of 3 ppm (2.5 mg/cu m). Additional studies by Largent [26] related to animal experiments; Kleinfeld [34] reported a fatal HF poisoning, without any exposure data; Heyroth's data [171] related to the highest concentration of hydrogen fluoride that could be tolerated by man for one minute. However, a second Largent study [172] reported by the Documentation reported that "some redness of the skin of the face was induced by exposure to the concentration of 3.39 ppm [2.8 mg/cu m] and by higher concentrations...." The Documentation presumed that prolonged inhalation of HF at high concentrations would lead to fluorosis.

The United States of America Standards Institute [173] (now referred to as ANSI) listed an 8-hour TWA concentration of 3 ppm (2.5 mg/cu m) as an acceptable standard (Z37.28-1966) for hydrogen fluoride. This TWA, according to ANSI, was supported by observations of animals exposed to HF by Stokinger [55] and Machle and co-workers [35,54] as well as supported in a review by Heyroth. [174] The United States of America Standards Institute [173] stated that an acceptable ceiling concentration had not been documented, but suggested that exposure be kept below 10 ppm.

Pennsylvania [175] adopted 3 ppm (2.5 mg/cu m) as both a TWA and a 15-minute short-term limit for HF. The short-term limit represented the maximum airborne concentration of a contaminant to which a worker might be exposed for 15 minutes, based on the assumption that there were sufficient recovery periods between episodes for recuperation. In <u>Short Term Limits for Exposure to Airborne Contaminants, A Documentation</u>, [176] Machle et al, [54] the 1966 Documentation, [169] and the Manufacturing Chemists' Association [2] were cited as supporting this short-term limit.

The following MAC values for HF have been set by foreign countries: Hungary and Poland, 0.5 mg/cu m [177]; East Germany and Czechoslovakia, 1 mg/cu m [177]; Yugoslavia, 1.7 mg/cu m [177]; Italy, [178] and Finland, [179] 2 mg/cu m. Bulgaria [179] listed a 1-mg/cu m permissible level. West Germany [180] and Britain [181] adopted a value of 2.5 mg/cu m. Hungary [177] also proposed a 1-mg/cu m peak, and Czechoslovakia [177] suggested a peak MAC of 2 mg/cu m.

In the Soviet Union, a mandatory maximum permissible concentration of 0.5 mg HF/cu m in the workroom air was established in 1959 by the Main State Health Inspector of the USSR. [182] The USSR allowed the permissible concentration to be exceeded if workers were in an industrial area for a brief, unspecified period.

In Japan in 1971, the Subcommittee on Permissible Concentrations of Hazardous Substances [183] recommended a permissible concentration for HF of 3 ppm (2.5 mg/cu m). This permissible concentration was an average concentration below which workers should not be adversely affected. In their documentation, [178] the Subcommittee reported that Japanese studies were insufficient, so the permissible concentration value of 3 ppm (2.5 mg/cu m), generally in use in Western European countries and the US, was chosen.

The present federal air contaminant limit (29 CFR 1910.1000) for hydrogen fluoride is an 8-hour TWA of 3 ppm (2.5 mg/cu m) based on the American National Standard Z37.28-1969 and published in the Federal Register 39:23543, June 27, 1974.

Basis for the Recommended Environmental Limit

The recommended occupational environmental limit for HF is expressed on a weight of HF/volume of air basis (mg/cu m). In evaluating the data presented, the ppm values in the cited literature have been converted to mg/cu m by assuming a molecular weight of 20 amu for HF. The basis of the limit is prevention of: (a) irritation of the skin, eyes, and respiratory tract; and (b) deleterious effects of skeletal fluorosis (increased bone density or osteosclerosis due to retention of fluoride).

The data collected by Largent [26] from human experimental studies are most relevant in establishing an environmental limit to prevent irritant effects. No noticeable adverse effects were found in one subject exposed for 15 days (6 hours/day, 5 days/week) to HF at concentrations which averaged 1.2 mg/cu m. Slight irritation of the exposed skin, eyes, and nose occurred in all five human subjects exposed for periods of up to 50 days at concentrations averaging between 2.1 and 3.9 mg/cu m, with ranges of concentrations between 1.5 and 6.5 mg/cu m. Slight desquamation of the superficial epithelium of the face was observed in one subject after several successive days of exposure to HF at 2.8 mg/cu m. No symptoms or signs of lower respiratory tract irritation occurred at any exposure levels. Comprehensive medical examinations before the exposures and at the end of each of the experiments did not detect adverse effects of any kind except for minor irritations which quickly subsided.

Hydrofluoric acid at concentrations of 25 mg/cu m could be tolerated by two human subjects for several minutes; only mild irritation of the eyes, nasal passages, and middle respiratory tract occurred. [35] Subjects did not cough during a 3-minute exposure. At 50 mg HF/cu m, these irritating effects were marked, and at 100 mg HF/cu m, the highest concentration of HF that was tolerated for more than one minute, there was immediate smarting of the exposed skin and marked eye and respiratory tract irritation.

Animal studies by Ronzani [52] showed that inhalation produced no adverse effects in rabbits, guinea pigs, and doves at an exposure level of 2.5 mg HF/cu m for 31 days. Stokinger [55] found only minor pulmonary changes in one out of five dogs exposed at 7 mg HF/cu m for 6 hours/day, 6 days/week, for 5 weeks. Renal and hepatic degenerative changes were reported by Machle and Kitzmiller [54] in rabbits, guinea pigs, and monkeys exposed at 15 mg HF/cu m for 6-8 hours daily, except weekends, until 309 hours had accumulated.

In man, kidney damage was only reported in severe, acute overexposures. [29,31] In a series of human HF inhalation experiments by Largent [26] with average exposure levels ranging from 1.2-3.89 mg HF/cu m for periods of up to 50 days, the lack of adverse effects on the kidneys was indicated by "normal" urinalyses.

The only epidemiologic study [49] reported which was designed to identify a chronic respiratory effect in workers exposed for many years to HF did not show any abnormal pulmonary function which was reasonably attributable to HF exposure. The averages of the observed values for FVC, FEV 1, and FEV 1/FVC from 305 chemical workers, including 11 HF workers (values for the HF workers were not separated) were within about 3% of the predicted values, with no significant difference between the chemical workers and a control group. The ratio of RV:TLVol was within normal limits for both groups. Determinations of HF in the air averaged about

1.03 ppm (0.85 mg/cu m), ranging from 0.07 to 10 ppm (0.06-8.2 mg/cu m).

The US Public Health Service [49] evaluated the effects of chemical irritants on exposed workers in a chemical plant where HF was one of the primary chemicals produced. Twenty-eight samples of airborne HF were taken with sampling periods ranging from 10 to 30 minutes. Results ranged from 0.07 to 10.0 ppm (0.06-8.2 mg/cu m), with a mean of 1.03 ppm (0.85 mg/cu m). Pulmonary function tests were performed on 305 chemical workers including 11 workers exposed to HF, and a control group of 88 workers in a box plant. The observed FVC, FEV 1, and FEV 1/FVC values for the total group were within about 3% of the predicted normal values with no significant difference between the chemical workers and the control group. The residual volume expressed as a percentage of total lung volume was 30.8% in the chemical workers, as contrasted with 26.8% for the box-plant workers, with both values within normal limits (35% being the upper limit of normal). The authors pointed out that this difference could be explained by the higher average age of the chemical workers, since RV:TLVol usually increases with advancing years.

Rye [45] reported that there was not a higher incidence of respiratory complaints in an unspecified number of phosphoric acid production workers when compared to a control group. According to the author, airborne concentrations of HF and silicon tetrafluoride were kept below 2.5 mg HF/cu m. One determination of airborne HF averaged 2.0 mg/cu m during an 8-hour period.

Correlation between airborne concentrations of HF and skeletal fluorosis has not been systematically investigated. Cases of osteosclerosis have been reported in workers exposed to HF, [37-41, HR

Henderson, written communication, September 1974] but no airborne concentrations were given. In at least two of the studies, [37,39] exposures apparently occurred to both gaseous and particulate fluorides. Considering the lack of any meaningful data for evaluating threshold airborne HF levels producing skeletal fluorosis, one has to refer to inorganic fluoride studies. Comparison of absorption and excretion of inhaled inorganic fluorides and HF [43] showed the same changes in the rate of urinary F excretion during and after exposure, indicating that the metabolism of absorbed F is the same whether the F is inhaled as inorganic fluoride or as HF. Based on this similarity of absorption, excretion, and, by inference, retention of F in osseous tissue, findings from inorganic fluoride studies can be applied in establishing an environmental limit for the prevention of osteosclerosis from HF exposure.

A study on inorganic fluorides relevant to the development of a workplace environmental standard is the one by Derryberry et al. [48] They provided comprehensive environmental and urinary F excretion data on each worker included in the survey and correlated it with radiologic findings. Environmental workplace fluoride levels were evaluated from approximately 750 air samples over a period of many years. An average daily fluoride exposure for each job was established, and from these data a weighted workplace airborne exposure was calculated for the period of employment of each worker. The range of individual average weighted exposures was 0.50-8.32 mg F/cu m, with 1.78-7.73 mg F/cu m being associated with minimal increased or questionable bone density (Table III-4). The difference in averages between the increased bone density group (average exposure 3.38 mg F/cu m) and the group with normal bone density (average exposure 2.62 mg

F/cu m) is significant by both t test ($t = -2.75$, $p = 0.0045$) and rank test ($Z = 2.2$, $p = 0.014$). The increased or questionable bone density was not associated with any musculoskeletal disability.

While the work of Derryberry et al [48] is helpful in developing a workplace environmental standard, it has inherent weaknesses which limit the extent to which the findings of the authors can be directly applied to the determination of a workplace environmental limit. The smallness of the test population placed limitations on the statistical significance of the findings. In the study, 17 out of 74 workers exposed to F at various concentrations were diagnosed as having bone density changes of minimal or questionable degree. The authors stated that these diagnoses were made by a radiologist who had prior knowledge that the tested individuals had potential fluoride exposures and who did not feel that the radiographs showed sufficient increase in bone density to be recognized as such in routine radiologic practice.

The Derryberry et al [48] study is of value, however, because it is comprehensive and it indicates that a threshold for minimal increases in bone density exists. From all aspects of the study, this threshold is best represented by an average exposure below 3.38 mg F/cu m.

In summary, studies by the US Public Health Service [49] and by Rye, [45] although limited in extent, suggest that no chronic pulmonary effects would be expected at exposure levels of 2.5 mg HF/cu m. The human experimental study by Largent [26] showed that only temporary, slight irritation of the skin, eyes, and nose resulted from exposure to HF at average concentrations of 2.12-3.89 mg/cu m. No signs or symptoms of lower respiratory tract irritation were reported at these average concentrations.

The study by Derryberry et al [48] indicates that exposures to HF somewhat below 3.38 mg F/cu m should prevent deleterious increases in bone density.

It is concluded that the recommended workplace environmental limit for HF of 2.5 mg/cu m as a TWA will provide protection of workers from the effects of HF over a working lifetime. In addition, in order to preclude acute irritation from HF, it is concluded that exposure of workers should not exceed 5 mg/cu m. Therefore, a ceiling limit of 5 mg HF/cu m based upon a 15-minute sampling period is proposed.

It is recognized that many workers handle small amounts of HF or are working in situations where, regardless of the amount used, there is only negligible contact with the substance. Under these conditions, it should not be necessary to comply with many of the provisions of the recommended standard, which has been prepared primarily to protect worker health under more hazardous circumstances. Concern for worker health requires that protective measures be instituted below the enforceable limit to ensure that exposures stay below that limit. For these reasons, "occupational exposure to HF" has been defined as exposure at or above half the workplace environmental limit, thereby delineating those work situations which do not require the expenditure of health resources for environmental and medical monitoring and associated recordkeeping. Half the environmental limit has been chosen on the basis of professional judgment, rather than on quantitative data that delineate nonhazardous areas from areas in which a hazard may exist. However, because of nonrespiratory hazards such as those leading to skin burns or irritation or eye contact, it is recommended that appropriate work practices and protective measures to limit such contact be required regardless of the air concentration.

It is recognized that slight irritation to the skin, eyes, and nose may occur at exposure levels below the recommended environmental limit. This possibility emphasizes the need for further study relating to the acute and chronic effects of HF on the skin, eyes, and respiratory system. In addition, several animal studies reported kidney damage [54,55,58] after exposures to HF at concentrations as low as 15 mg/cu m. [54] These studies reveal a need for additional information regarding human exposures, and the possible acute or chronic effects of HF on the renal system.

Basis for Biologic Monitoring

Since the deposition of the F ion in the osseous system requires transport via the circulatory system (excluding topical application to the teeth), F is found in some physiologic fluids, eg, in blood and urine. This fact, combined with the fact that the urinary F concentration can be related to the onset of osteofluorosis, [HR Henderson, written communication, September 1974, 48,50] provides the basis for the recommendation that biologic monitoring of workers exposed to HF be performed as an acceptable means of identifying workers at risk. In the case of fluoride exposure (HF and associated gaseous and particulate inorganic fluorides), determination of airborne HF is not an entirely satisfactory alternative procedure as it is not feasible to estimate the quantity of F ingested by each worker. One may generalize that good personal hygiene will minimize the problem of F ingestion, but the quantity ingested is small, a few mg/day, as shown by the data supporting the recommended workplace environmental limit. Occupational exposure to HF and F is not the only source of F intake, food and fluoride in water are also influencing factors. Furthermore, unless the air sampling program included all employees at all times of exposure, it would be necessary to assume that exposure conditions at the time of sampling would be representative of exposure conditions when no sampling was conducted, which may not be the case. Biologic monitoring allows for the determination of total F excretion and therefore provides an indication of total fluoride intake. This serves as a means of spotting breakdowns in engineering controls and work practices. NIOSH therefore concludes that biologic monitoring shall be a part of the total worker protection program.

(a) Postshift Urinary F Biologic Standard

Several studies [26,43,45] demonstrated a rapid rise in urinary F excretion, within 2 hours of exposure to HF, which remained at high levels for 2-4 hours after cessation of exposure. Thus, end-of-shift urine samples, as recommended by NIOSH, will reflect exposure conditions occurring during the working day. Although this fact is not relevant to the correlation of postshift urinary F excretion with osteofluorosis, it does provide a means of monitoring employee work practices and engineering control measures.

Unfortunately, insufficient HF data are available to correlate osteofluorosis with postshift urinary F excretion. As with the establishing of the environmental limit, one has to rely on inorganic fluoride data. Collings et al [43] demonstrated that inhalation of HF and inorganic fluorides gave similar results both in regard to the rapidity with which urinary F excretion increased, and in relation to the extent of the increase in amounts of fluoride excreted in the urine. The study by Derryberry et al [48] provided long-term individual worker postshift urinary F excretion data which can be related to reported cases of increased bone density. In this study, average postshift urinary F levels of workers were determined from an average of 38 urine specimens for each worker. The data from this study demonstrated that, as the average urinary F excretion level increased, the percentage of cases of minimal or questionable increase in bone density gradually became greater until excretion in the range of 8-8.9 mg F/liter was reached; at this point, 60% of the group excreting F in that range showed minimal or questionable bone density increases (Table III-5).

Kaltreider et al [50] found osteofluorosis in 76 of 79 aluminum potroom workers. Urinary spot samples collected during working days showed an average F excretion of 8.7 mg F/liter for pot tenders, 9.8 mg F/liter for tapper-carbon changers, and 9.6 mg F/liter for cranemen. In a later study [50] at a different aluminum plant, no cases of increased bone density in a group of 231 potroom workers were found. Averages of postshift urinary F concentrations taken on the last day of the workweek over a 5-year period and corrected to a specific gravity of 1.024 ranged from 3.0 to 10.4 mg F/liter.

Largent et al [38] reported three workers with "slight" skeletal fluorosis who had been exposed to HF. The average postshift urinary F concentrations of these workers over a 3-year period were 10.09, 10.62, and 12.29 mg F/liter, respectively.

Four workers engaged in the production of HF [49] who had no osteofluorosis discernable by radiologic examinations had average urinary postshift F excretions of 4.31, 6.85, 17.5, and 26.6 mg/liter over a 5-day period. One of the two workers with high urinary F levels was exposed to a "gas out" during the week of urine collection and the other worker was exposed to a "reboiler leak." Although the determinations of F concentrations in these urine samples, taken only for a 1-week period, are of little value in establishing a postshift urinary F biologic standard, they nevertheless demonstrate that end-of-shift urine samples reflect exposure conditions. One of the four workers (HR Henderson, written communication, September 1974) showed "first-degree" osteofluorosis on follow-up examinations 2 years later. His average postshift urinary F level over a period of 7 years was 11.5 mg/liter.

The data provided, although limited, indicate that a postshift urinary F level, averaged over an extended period of time, of less than 8 mg/liter, as recommended by NIOSH, will not lead to osteofluorosis, although a minimal or questionable increase in bone density might develop after many years of occupational exposure. It is concluded that a postshift urinary biologic standard of 7.0 mg F/liter corrected to a specific gravity of 1.024 will provide an acceptable margin of safety.

(b) Preshift Urinary F Biologic Standard

Upon cessation of F exposure, the initial rapid rise of urinary F concentration is followed by a return to stable and relatively low levels of urinary F excretion within about 24 hours. [43,45] Urinary F concentrations approached preexposure values within 1-6 days. [43-45] These studies reveal that (1) the time required for the preshift sample to stabilize is quantitatively related to the urinary F concentration in the postshift sample, and (2) urinary F analyses conducted before exposure (preshift), as recommended by NIOSH, and after a nonexposure period of 1 day or more will provide a stable baseline value indicative of a worker's residual F retention (body burden).

The precise relationship of the concentration of fluoride in the preshift urine sample to the onset of osteofluorosis has not been sufficiently demonstrated, but a limited number of industrial exposure studies [49,50, HR Henderson, written communication, September 1974] as well as one nonindustrial exposure study [184] enable some inferences to be drawn regarding the relationship of osteofluorosis to the preshift urine sample.

Preshift urinary F excretions were analyzed [49] in 25 chemical workers exposed to HF or particulate fluorides in concentrations ranging from 0.077 to 10.0 ppm (HF) and 0.1-0.49 mg/cu m (particulate F). Preshift urine specimens, which were collected after the workers had been away from the plant on their days off, had F concentrations that ranged from 0.33 to 4.48 mg F/liter. Corresponding levels for a control group of 10 office workers not exposed to HF or particulate fluorides were 0.5-1.88 mg F/liter.

Additional data on environmental and urinary F levels of the same plant population were made available by the company (HR Henderson, written communication, September 1974). Periodic urinary F determinations on 13 HF workers over a 10-year period indicated that the average preshift levels for the workmen ranged from 2.0 to 5.7 mg/liter. One of four workers with high postshift urinary F concentrations whose X-rays did not indicate osteosclerosis when he was examined 2 years earlier demonstrated minimal osteosclerosis upon a follow-up examination. His average preshift urinary

F level was 5.3 mg/liter, ranging from 2.6 to 16.3 mg F/liter.

No osteofluorosis was found in a group of 147 potroom workers excreting 1.4 mg F/liter of urine (calculated as a preshift average) ranging from 0 to 11.9 F/liter. [50] Urine samples were collected after the workers were off work for 48 hours. The results were corrected to a specific gravity of 1,024.

Stevenson and Watson [184] reviewed medical records of patients residing primarily in Texas and Oklahoma where drinking water supplies contained up to 8 ppm fluoride. A diagnosis of fluoride osteosclerosis was made in 23 patients living in communities whose drinking water supplies contained 4-8 ppm fluoride. It was concluded that fluoride osteosclerosis did not develop in patients who drank water with a F concentration of less than 4 ppm.

The preceding data [49,50, HR Henderson written communication, September 1974] suggest that preshift urinary values up to 5.3 mg F/liter were not associated with osteofluorosis. While the findings of the nonindustrial exposure study [184] cannot be strictly applied to the determination of a preshift level, the results of the study indicate that a preshift level below 5.3 is desirable. It is concluded that a preshift level of 4 mg/liter will provide adequate worker protection. The validity of the value, as a preshift level, should be tested and adjusted in the future as more information is gained.

(c) Urine Specific Gravity

Urinary fluoride levels should be corrected to a uniform specific gravity of 1.024 to compensate as adequately as possible for various dilutions of urine samples and for the impracticality of collecting 24-hour specimens. Elkins et al [185] concluded that, although the true mean value for specific gravity is probably 1.022, the value most widely used for specific gravity correction in the US is 1.024, and it should continue as a reference to enable data comparisons among different investigators.

Basis for Radiologic Examination

The early signs of increased bone density from F absorption are most apparent in the lumbar spine and pelvis. [39] Since changes in the osseous system may be the only evidence of increased absorption and retention of fluorides, periodic X-ray examination of the pelvis may be valuable in cases where urinary F levels have been found to be high. It should be noted that the first changes produced by fluoride absorption and retention are difficult to recognize without prior knowledge that the individual had a fluoride exposure. Radiologic examination of the pelvis can result in irradiation of the gonads and embryos. [186] This may lead to deviation from normal mutation rates and may produce developmental abnormalities in the human embryo. Because of the difficulty of ensuring adequate protection for female gonads and for embryos, it is recommended that radiologic examination of the female pelvis not be conducted. Since male gonads can be protected adequately during pelvic X-ray examination, preplacement male pelvic examinations should be considered to obtain baseline radiologic information.

VI. WORK PRACTICES

Safety precautions for handling anhydrous hydrogen fluoride (HF) are the subject of a considerable body of literature. [1,2,4,12,187-197] Less has been written on the handling of aqueous solutions of hydrogen fluoride (HF acid), particularly in low concentrations, although the problems and health effects from use of the two forms are essentially similar. [1,2,189,190,198,199] A major portion of the literature deals with work practices for the safe handling of HF in the alkylation process in petroleum refining and detergent manufacturing. [12,187,188,191,193,195] In general, stress is placed on proper plant design as the fundamental preventive measure, followed by precautionary use of respiratory, eye, and skin protection which vary in complexity depending on the degree of potential exposure. Other work practices receiving emphasis in the alkylation process are training and drills; distinctive identification of HF areas, tools, and plant equipment used for HF work; neutralization and inspection of all protective equipment, tools, and plant equipment before handling by unprotected personnel; neutralization of waste prior to disposal; and precautions necessary for the prevention of fire and explosion due to hydrogen generated by contact of metals with hydrogen fluoride. While these work practices have been described in connection with alkylation processes, they appear to be readily adaptable to other similar processes using HF.

Reports of work practices written specifically for the prevention of low-level exposures are limited. Handling of hydrogen fluoride in enclosed systems was recommended. [200] Recommendations have also been made for the control of hydrogen fluoride exposures by using ventilation devices such as laboratory hoods, [1] using open construction practices, [187,196] using compressed air or portable air movers, [191] including natural or forced draft ventilation for work areas in plant design, [2] and using ventilation for hydrogen fluoride storage areas. [190] Ventilation systems should be designed and constructed to be corrosion-resistant and safeguards should be provided to prevent condensate from dripping onto workers. [2,190] Discharges from ventilating systems should not be located near fresh air intakes, equipment subject to corrosion by HF, or building exits or entrances. [2,190] In general, where equipment or processes containing hydrogen fluoride cannot be completely enclosed, good engineering practices should be used to control continuous low-level exposures and to minimize excursions. Good ventilation practices are recommended in the current edition [201] of Industrial Ventilation--A Manual of Recommended Practice published by the American Conference of Governmental Industrial Hygienists.

(a) Skin and Eye Protection

The severity of skin burns caused by contact with hydrogen fluoride has been extensively described. [1,22,24,25,32,188,194] Documentation of serious eye injuries due to exposure to hydrogen fluoride has been sparse [28,26,27] although it has been frequently stated without further elaboration [1,2,4,187,189,190,202] that hydrogen fluoride is a severe eye hazard. Mayer and Guelich [32] stated that burns from weak HF acid (1-20%) were not noticeable for several hours. No supporting data were given for this statement, but Largent [26] reported experiments which indicated that airborne HF concentrations averaging 2.59-4.74 ppm caused noticeable skin and eye irritation. On the basis of good practice, appropriate skin and eye protective devices should therefore be worn when airborne concentrations of HF are likely to exceed the recommended workplace environmental limit, or when direct contact with HF or HF acid may occur.

What constitutes appropriate skin and eye protection is a subject of some complexity, depending on the particular process or operation involved, and the degree of potential hazard. Literature dealing with the use of HF in alkylation processes [187,188,191,193,195,203] listed 3-4 classes of protective clothing required for various process operations. References [1,2,4,46,189,194,196] dealing with less specific potential exposures to hydrogen fluoride were correspondingly less specific in their recommendations for protective clothing, but stressed the importance of complete skin coverage when working with or around hydrogen fluoride. Table VI-1 is a guide for selection of proper protective clothing. Considerable emphasis was placed in the development of this guide on the potential for skin burns caused by pinholes in impervious gloves, and it is of utmost importance to inspect gloves and other protective clothing prior to issue. [1,192,194,196,197] Care must be taken in removing protective clothing and equipment after use where hydrogen fluoride is present. The possibility of self-contamination if the clothing and equipment are removed in the wrong order and without thorough washing cannot be ignored. A written procedure for such removal must be prepared and enforced after proper employee instruction in its provisions. [189,190] After removal, protective clothing and equipment must be neutralized, washed, sanitized, and inspected prior to storage and reissue. Those handling the clothing and equipment prior to neutralization must themselves be protected. [1,188,189,191-196] In some cases, it may be appropriate for identification purposes to use distinctive coloring for protective clothing worn in the presence of hydrogen fluoride. [187] Protective clothing made of porous materials, eg, cotton, must not be used [32] since it can become saturated with hydrogen fluoride with subsequent revaporization, thus causing an inhalation hazard to the wearer. Protective clothing must be made of neoprene, plasticized polyvinyl chloride or of an equally impervious material. [2]

Wherever skin and eye contact with hydrogen fluoride may occur, it is essential that adequate sources of water for washing are available.

TABLE VI-1

PROTECTIVE CLOTHING SELECTION GUIDE

Examples of Type of Operation	Protective Clothing and Equipment
Receiving and neutralizing protective clothing, safety equipment, tools Laboratory operations with aqueous hydrogen fluoride in a ventilated hood, eg, pouring, heating, observing reactions Photoetching	Chemical goggles, face shield, impervious gloves, impervious apron, shoe covers or overshoes
Electroplating operations using hydrogen fluoride solutions	Same as above, except impervious boots instead of overshoes
In association with hydrogen fluoride systems or equipment, routine operating work or maintenance of nonacid equipment, reading instruments, operating valves in closed systems, reassembly of thoroughly cleaned acid equipment Inspections of hydrogen fluoride hazard areas by supervisors or visitors Entering low concentrations of acid vapor	Impervious head and neck covering (hood) or chemical goggles and face shields, impervious gloves, impervious overshoes or boots

TABLE VI-1 (CONTINUED)

PROTECTIVE CLOTHING SELECTION GUIDE

Examples of Type of Operation	Protective Clothing and Equipment
Nonroutine operations associated with hydrogen fluoride systems or equipment, repair operations not involving the opening of acid-bearing equipment, washing down, start-up or shut-down of plant sections, assembling of acid equipment not thoroughly neutralized, greasing valves Mixing or adding hydrofluoric acid to electroplating solutions	Impervious head and neck covering (hood), or chemical goggles and face shield, impervious gloves, impervious jacket and trousers, boots
Sampling hydrogen fluoride, opening HF acid equipment, dismantling valves and pumps contaminated with hydrogen fluoride, breaking unions, opening meters, connecting or disconnecting tank cars or cylinders, venting hydrogen fluoride containers	Impervious head and neck covering (hood), impervious jacket and trousers, impervious gloves, boots, plus air-supplied respirator as specified in Table I-1
Entering vessels, repairing hydrogen fluoride leaks, emergency operations, clean-up of spills, entering high concentrations of acid vapor or sprays of acid	(1) Impervious gloves; impervious boots, continuous-flow air-supplied impervious suit with body harness and safety line, if required, and auxiliary self-contained air supply (2) Impervious full-body suit and self-contained positive-pressure full-facepiece breathing apparatus, as specified in Table I-1

[1,2,4,32,188-194] The most important first-aid measure for skin or eye contact with hydrogen fluoride is immediate flushing with water, which must be continued until medical assistance is obtained. Eyewash fountains and safety showers with quick-acting valves must be located at strategic points near hydrogen fluoride work areas. When washing eyes after contact with HF, it may be necessary to hold the eyelids open to ensure complete washing. Safety showers should be equipped with automatic alarms to indicate use and summon aid. [12,188,194] The use of warm water for washing contaminated skin has been suggested to prevent shock, [12,187,191] while cold or iced water has been suggested to alleviate pain. [1,2, 4,193] In any case, hydrogen fluoride must be flushed from the skin without the delay caused by searching for water of a particular temperature. Immediate flushing is important to prevent deep penetration of hydrogen fluoride under the skin.

Eye protection must consist of chemical-type goggles with hooded ventilation openings in addition to face shields if eyes and face are not protected by respiratory protection. Since contact lenses prevent effective eye irrigation, they must not be worn in the vicinity of hydrogen fluoride.

(b) Respiratory Protection

Canisters used with respirators have limitations:

(1) They do not protect in atmospheres deficient in oxygen.

(2) The capacity of the canister to absorb hydrogen fluoride is limited by factors of concentration of hydrogen fluoride, breathing rate of the wearer, temperature, and humidity. [204] 30 CFR 11 lists maximum use concentrations in percent by volume for various types of gas masks:

Acid-gas front- or back-mounted gas mask: 2% (20,000 ppm)
Acid-gas chin-style gas mask: 0.5% (5000 ppm)
Acid-gas escape mask: 0.1% (1000 ppm)

(3) Canisters have limited shelf life. Canisters must be replaced after each use and at the expiration of the shelf life recommended by the manufacturer.

If the odor of hydrogen fluoride becomes noticeable while wearing a gas mask, the hydrogen fluoride concentration is too high for safety, the mask is not properly fitted, or the canister is not effective. If the odor is noticeable, the area should be left without delay. Canister masks are not suitable [2,204] for use in emergencies because the concentration of hydrogen fluoride may be unknown, or an oxygen deficiency may exist. Because of the severe effects of hydrogen fluoride on skin, only full-face respiratory protection may be worn.

(c) Fire and Explosion

Hydrogen fluoride is nonflammable and will not promote ignition in contact with organic material. [2] In contact with metals, however, hydrogen fluoride can generate hydrogen which can be an explosion and fire hazard. [2,189,190,198,205,206] Metal containers of hydrogen fluoride must be vented regularly to prevent accumulation of hydrogen. [189,190] Sources of ignition must not be present during, such venting and ventilation must be provided for removal of any hydrogen released. [2,189,190] Repairs to hydrogen fluoride systems involving cutting or welding must be preceded by purging with inert gas or dry air, keeping the systems hydrogen-free during the repair process. [2,189]

Metal containers which have contained hydrogen fluoride must never be washed out with water, since this destroys the passivation (a nonreactive coating caused by reaction of the HF and container) and allows hydrogen to be formed. [189,190,2,187,194] Sparkproof tools must be used in opening tank cars and metal containers to prevent ignition of hydrogen. [2]

Ziehlke et al [207] reported on the explosive rupture of an HF cylinder due to prolonged storage and consequent corrosion and leakage.

They reported that the date of the last test of the cylinder was October 1955, and the explosion occurred in June 1969. Recommended preventive measures [207] included limiting reserves of hydrogen fluoride to required amounts, periodic examination for leakage and deterioration, observance of the 5-year retest limitations (49 CFR 173.34, 49 CFR 173.264), venting for reduction of hydrogen pressure, and use of inert gases instead of air for pressure transfer of HF from containers. A 4-month limitation on storage of cylinders has been recommended. [189]

(d) Leaks and Spills

Leaks and spills of hydrogen fluoride present a serious problem because of hazards to personnel, corrosion of materials, and difficulty of safe disposal. Detection of leaks is reasonably simple as HF fumes visibly in moist air, [4,187,188,191] and fuming is also readily detectable above HF acid of greater concentration than 48%. [2] Small leaks can be detected by holding an open bottle of concentrated aqueous ammonia near the suspected site of the leak [4] and observing the white fume formed if hydrogen fluoride or other acid gases are present. The strongly irritating and pungent odor [2,187,188,191] of hydrogen fluoride may be indicative of leaks. Early warning of leaks has been facilitated by painting flanged connections in hydrogen fluoride piping with a special acid-indicating paint which changes color in contact with the acid. [195,203] Regular inspection was recommended for early leak detection. [188,194,203] Use of length-of-stain detector tubes near locations of possible leaks for leak detection has been recommended. [188] Where water is used for cooling, for example in heat exchangers, leaks of hydrogen fluoride may be detected by the measurement of the conductivity or pH of the cooling water. [191,195]

When leaks or spills are detected, immediate control is imperative, followed by safe disposal of the hydrogen fluoride. Workmen repairing leaks or cleaning up spills should work on the windward side, if possible, or air-movers may be used to blow the acid gases away from the workmen. [2,191] Complete protective clothing is required for those controlling leaks and spills. [188,190,191,193] Areas in which significant quantities of hydrogen fluoride are located should be surrounded by raised curbs to confine spills [187,188,191,195] and to delineate the hazardous area. Curbs may be emphasized by painting them a distinctive color. [12,187,188,191,193] Floors of hydrogen fluoride areas should be constructed of concrete, or the areas should be covered with a neutralizing material, such as a layer of oyster shell or limestone. [12] Floors should slope to drains leading to neutralizing pits. [187,191,195] Lime or limestone may be used to neutralize waste hydrogen fluoride in these pits, [187,191,195] or soda ash may be used. [2] However, the latter produces sodium fluoride, which is toxic to warm-blooded animals, [2] and may cause a foaming reaction that may be undesirable. Accordingly, such neutralizing pits must be isolated and secured against entry by animals or unauthorized personnel. Pit alkalinity should be checked daily [187] to ensure sufficient neutralizing power for emergencies. Spills should be neutralized, then washed into drains, [2,194] or washed into the pits and then neutralized. [2,4,191] Pools of runoff from washdown of spills should be guarded until neutralized. [198,205,206] Small spills of hydrogen fluoride can be greatly diluted and flushed into sewers with large quantities of water. [2]

Leaking cylinders should be removed to the outdoors or to isolated well-ventilated areas. The cylinder contents should be transferred to a more suitable container or disposed of by routing to a neutralizing or reaction vessel, when the process system is so designed, or in any other safe manner. [2,4]

(e) Materials of Construction

The corrosion of metals by hydrogen fluoride varies with the concentration of HF. Accordingly, materials suitable for anhydrous HF containers, for example, may not be suitable for HF acid. Fehr [192,194] reported that the corrosive characteristics of hydrofluoric acid changed as the concentration increased from 65 to 80%; below 65% it had a low corrosion rate on lead, while above 65% it rapidly attacked lead. Below 60% it has a high corrosion rate on steel, while, above 80%, practically no action occurred on steel. Fehr [192,194] also stated that rubber, Neoprene, and many plastics showed excellent resistance to weak hydrofluoric acid, but were increasingly attacked at concentrations above 60% and 80% in aqueous solutions. He reported satisfactory use of steel for handling anhydrous hydrogen fluoride. Materials containing silica, eg, cast iron, glass, and asbestos, were unsatisfactory. In 1950, Whitaker [208] reported on materials used in plants manufacturing hydrogen fluoride. He substantiated the satisfactory performance of mild steel for storage tanks and cylinders for HF. Experiments with HF acid showed that 60% acid caused excessive pressure in drums, due to hydrogen formation, even though the drums had been passivated. When the acid concentration was increased to 65%, no pressure was produced in passivated or in new, unpassivated drums. Further experiments showed [208] that there was a breakpoint near

64% below which steel was undesirable as a container for HF acid. The Manufacturing Chemists' Association [2] stated that 70% HF acid exerts an effect on steel adequate to passivate containers for packaging and transportation purposes.

Containers for HF and HF acid are specified in 49 CFR 173.264. In general, HF acid of less than 70% concentration may be packed and shipped in rubber, wax, polyethylene or other HF-acid-resistant material in wooden or fiberboard boxes, or unlined steel tank motor vehicles; HF acid of between 60-80% strength can be shipped in unlined metal barrels, drums, or tanks, provided they have been properly passivated; HF acid of less than 65% strength can be shipped in rubber drums; HF acid of less than 62% strength can be shipped in lined metal barrels or drums (lining not specified, but must pass prescribed tests); HF acid of less than 40% strength can be shipped in rubber-lined tank cars; while anhydrous hydrogen fluoride may be shipped in steel cylinders, tank cars, tank motor vehicles, or portable tanks. A comprehensive list of materials of construction for hydrofluoric acid was listed by the Manufacturing Chemists' Association, [2] while steel is generally used for handling and storing anhydrous hydrogen fluoride. [2]

Porous materials, such as concrete, wood, pipe insulation, or plaster, absorb hydrogen fluoride and present a hazard until thoroughly neutralized or disposed of in a safe manner. [2,189,194] Cotton clothing readily absorbs hydrogen fluoride. [32] It can become saturated after long exposure, becoming a source of HF which may be an inhalation hazard to the wearer. Accordingly, cotton clothing should not be worn around HF processes.

(f) Storage

Hydrogen fluoride containers stored for extended periods of time may develop cracks; corrosion may occur due to loss of passivation. Hydrogen generated because of loss of passivation can produce excessive pressure and rupturing of the weakened container. [207] The National Safety Council [189] recommends a 4-month maximum storage time for HF cylinders, while the Manufacturing Chemists' Association [2] recommends a maximum storage time of 90 days for unlined steel drums of HF acid. Accordingly, users of hydrogen fluoride must ensure that stocks on hand are limited to amounts required for current use, and that containers are used on a first-in, first-out (FIFO) basis.

Vents for HF storage tanks must be connected to an acid-absorption system so that HF cannot escape, causing a hazard. Such vents must never be connected directly to a container of liquid because of the danger of suck-back, with possible violent results. [2,187]

Drums or other containers of HF must be stored with the closures up to facilitate venting and prevent discharge of liquid during venting operations. [189] Hydrogen fluoride must be stored in cool, well-ventilated areas, out of the direct rays of the sun and away from other sources of heat. [1,2,4,189,190,199] Personal protective equipment must be worn when venting HF containers. [2] Venting should be performed on receipt and at weekly intervals, [2,190] using sparkproof tools.

Under no circumstances must hydrogen fluoride ever be stored or placed in containers having siliceous material as a component. Meyer [199] reported accidents due to perforation of polyester-bonded glass-fiber tanks containing solutions of hydrogen fluoride. Mayer and Guelich [32] described the deaths of two workmen who were splashed with hydrofluoric acid from a 5-pint glass bottle which had inadvertently been filled with 70% hydrofluoric acid. The gases generated by the reaction of hydrogen fluoride with the glass caused sufficient pressure to rupture the bottle.

(g) Training and Drills

Federal Occupational Safety and Health Standards, 29 CFR 1910.134, require training in the use of respiratory protection. Other references [2,12,189,190,193,195] stress the importance of training and drills for emergency situations. Accordingly, a requirement for training and drills is recommended. Trusty [12] recommended that those physicians who are unfamiliar with the medical management of hydrogen fluoride emergencies and likely to be called upon for HF emergency work be instructed in the proper procedures. He stressed the importance of properly advising the physician of the nature of the emergency so that proper treatment could be instituted.

(h) General Handling Precautions

Tools and equipment which have been used on hydrogen fluoride systems, or have been in contact with hydrogen fluoride, must be washed thoroughly and neutralized before being handled by unprotected personnel. [2,187,188,190,191,194] Such tools and equipment must be identified as potentially hazardous by being marked or painted a distinctive color. [194] Entry into areas restricted because of the presence of hydrogen fluoride must be controlled by a permit system. Permits must be issued by a responsible person, designated by management, who must also be responsible for determining the type of protective clothing required for entry. [12,188,191,193,195]

(i) Labeling

Trevethick [1] stated that solutions of HF acid at concentrations of 40% or above emit extremely irritating and toxic "fumes." The Manufacturing Chemists' Association [2] stated that solutions of HF acid above 48% HF emit "fumes." It appears, therefore, that solutions of HF of these concentrations or above would present an immediate inhalation hazard when handled or used. Dilute solutions in contact with the skin may have a delayed effect, while solutions of higher concentrations will have an immediate effect, as discussed above. Therefore, a separation of aqueous hydrogen fluoride solutions at the 40% concentration has been made for the purpose of ensuring proper precautionary labeling.

VII. COMPATIBILITY WITH EMISSION STANDARDS

There is presently no federal ambient air standard for hydrogen fluoride. A number of states have promulgated standards [209-213] for control of emission of fluorides. For example, Wyoming has adopted a fluoride regulation which states [209] that fluorides measured as HF in the ambient air shall not exceed 0.80 μg/cu m or 1.0 ppb (part per billion) as a 24-hour average. Pennsylvania's standard [210] sets the limit for fluorides (total soluble as HF) as 5 μg/cu m averaged over 24 hours. Montana's limit is 1 ppb (0.8 μg/cu m) as HF. [211] Washington [212] and New York [213] set two standards, one for forage and one for ambient air. In Washington, concentration of F in forage by dry weight (calculated as F ion) is not to exceed 40 ppm averaged over 12 consecutive months, 60 ppm averaged over 2 months, and 80 ppm more than once in any 2 consecutive months. Gaseous fluorides in ambient air, calculated as HF, are not to exceed 3.7 μg/cu m, averaged over 12 hours, 2.9 μg/cu m for 24 hours, 1.7 μg/cu m averaged over 7 days, 0.84 μg/cu m averaged over 30 days, and 0.5 μg/cu m averaged over the period March 1 through October 31 of any year. In New York, concentration of F in forage by dry weight (as F ion) is not to exceed 40 ppm averaged over a growing season not to exceed 6 months, 60 ppm averaged over 60 days, and 80 ppm averaged over any 30-day period. Gaseous fluorides, calculated as F ion, are not to exceed a 12-hour average of 4.5 ppb (3.7 μg/cu m), 3.5 ppb (2.85 μg/cu m) per 24-hours, 2.0 ppb (1.65 μg/cu m) averaged over 1 week and 1.0 ppb (0.8 μg/cu m) averaged over 1 month. The American Industrial Hygiene Association [214] recommended a Community Air Quality Guide for HF of 4.5 ppb (0.0036 mg/cu m) for 12 hours, 3.5 ppb (0.0028 mg/cu m) for 24 hours, 2.0 ppb (0.0016 mg/cu m) for 1 week, and 1.0 ppb (0.0008 mg/cu m) for 1 month.

These standards were not established on the basis of protection of human health, but on the basis of damage to livestock and vegetation. The levels established are well below those found to adversely affect human health.

Standards for fluorides in effluent from aluminum smelting operations have been proposed by the Environmental Protection Agency in the Federal Register 38(230):33170-83, dated 30 November 1973. The proposed 40 CFR 421 specified various concentrations of fluoride in effluent ranging from 0.05 kg/1000 kg of product/day to 2.0 kg/1000 kg of product/day, depending on the process and the technology used. These limits were apparently not based on biologic effects, but on the best practicable, or best available, technology.

Since these limits are not based on human health effects, they are not directly comparable with the recommended standard of Chapter I.

VIII. REFERENCES

1. Trevethick RA: Environmental and Industrial Health Hazards--A Practical Guide. London, William Heinemann Medical Books Ltd, 1973, pp 84-87

2. Hydrofluoric Acid, Chemical Safety Data Sheet SD-25, Rev 1970. Washington, DC, Manufacturing Chemists' Association Inc, 1970

3. Grogan RM: Fluorspar and cryolite, in Industrial Minerals and Rocks (Nonmetallics other than Fuels), ed 3 rev. New York, American Institute of Mining, Metallurgical and Petroleum Engineers, 1960, pp 363-82

4. Matheson Gas Data Book, ed 5. East Rutherford, New Jersey, Matheson Gas Products, 1971, pp 305-09

5. Weast RC (ed): Handbook of Chemistry and Physics--A Ready-Reference Book of Chemical Data, ed 53. Cleveland, CRC Press, 1972

6. Simons JH: Hydrogen fluoride--The catalyst--Pt I: Its physical and chemical properties. Pet Refiner 22:83-89, 1943

7. Simons JH: Hydrogen fluoride and its solutions. Chem Rev 8:213-35, 1931

8. Long RW, Hildebrand JH, Morrell WE: Polymerization of gaseous hydrogen and deuterium fluorides. J Am Chem Soc 65:182-87, 1943

9. Ricca PM: Exposure criteria for fluorine rocket propellants. Arch Environ Health 12:399-407, 1966

10. Hydrogen fluoride, Hygienic Guide Series, 2d printing, April 1964. Detroit, Mich, Am Ind Hyg Assoc, 1964

11. Scheele CW: Investigation of fluor spar and its acid, in The Collected Papers of Carl Wilhelm Scheele. New York, Kraus Reprint Co, 1971, pp 3-16

12. Trusty AW: Safety with hydrofluoric acid alkylation. Pet Refiner 23:469-71, 1944

13. Wood HB: Fluorspar and cryolite, in Minerals Yearbook, vol 1, Metals, Minerals, and Fuels. US Dept of Interior, Bureau of Mines, 1973, pp 517-30

14. Manufacturing Chemists' Association: Statistical Summary 1973--Suppl to Chemical Statistics Handbook, ed 7. Washington, DC, Manufacturing Chemists' Association, Sept 1973, pp 16-17,19-21, 23-24,36

15. Current Industrial Reports--Inorganic Chemicals 1972. Series: M28A(72)-14. US Dept of Commerce, Bureau of the Census, 1973, pp 5,25

16. Hydrofluoric Acid Makers Enjoy Good Times. Chem Eng News 53:8-9, 1975

17. MacMillan RT: Fluorine, in Mineral Facts and Problems, bulletin 650. US Dept of Interior, Bureau of Mines, 1970, pp 989-1000

18. HF consumption at 500,000 tons foreseen in 1977. Chem Mark Rep 201:3,47, May 8, 1972

19. Sadilova MS: [Material for standardization of the maximum permissible concentration of hydrogen fluoride in the air of populated areas.] Biol Deistvie Gig Znach Atmos Zagryaz 10:186-201, 1967 (Rus)

20. Lindberg ZY: [The combined effect of hydrogen fluoride and sulfur dioxide on the body of man and animals. Biol Deistvie Gig Znach Atmos Zagryaz 11:32-43, 1968 (Rus)

21. Browne TD: The treatment of hydrofluoric acid burns. J Soc Occup Med 24:80-89, 1974

22. Jones AT: The treatment of hydrofluoric acid burns. J Ind Hyg Toxicol 21:205-12, 1939

23. Dale RH: Treatment of hydrofluoric acid burns. Br Med J 1:728-32, 1951

24. Klauder JV, Shelanski L, Gabriel K: Industrial uses of compounds of fluorine and oxalic acid. Arch Ind Health 12:412-19, 1955

25. Dibbell DG, Iverson RE, Jones W, Laub DR, Madison MS: Hydrofluoric acid burns of the hand. J Bone Joint Surg 52:931-36, 1970

26. Largent EJ: Fluorosis--The health aspects of fluorine compounds. Columbus, Ohio State University Press, 1961, pp 34-39,43-48

27. McLaughlin RS: Chemical burns of the human cornea. Am J Ophthalmol 29:1355-62, 1946

28. Bertuna S: Treatment of HF burns with hyamine--Case report. Med Bull (Exxon) 29:270-77, 1969

29. Burke WJ, Hoegg UR, Phillips RE: Systemic fluoride poisoning resulting from a fluoride skin burn. J Occup Med 15:39-41, 1973

30. Hall LL, Smith FA, De Lopez OH, Gardner DE: Direct potentiometric determination of total ionic fluoride in biological fluids. Clin Chem 18:1455-58, 1972

31. Dieffenbacher PF, Thompson JH: Burns from exposure to anhydrous hydrofluoric acid. J Occup Med 4:325-26, 1962

32. Mayer L, Guelich J: Hydrogen fluoride (HF) inhalation and burns. Arch Environ Health 7:445-47, 1963

33. Greendyke RM, Hodge HC: Accidental death due to hydrofluoric acid. J Forensic Sci 9:383-90, 1964

34. Kleinfeld M: Acute pulmonary edema of chemical origin. Arch Environ Health 10:942-46, 1965

35. Machle W, Thamann F, Kitzmiller K, Cholak J: The effects of the inhalation of hydrogen fluoride--I. The response following exposure to high concentrations. J Ind Hyg 16:129-45, 1934

36. Elkins HB: The Chemistry of Industrial Toxicology, ed 2. New York, John Wiley & Sons Inc, 1959, pp 71-73

37. Wilkie J: Two cases of fluorine osteosclerosis. Br J Radiol 13:213-17, 1940

38. Largent EJ, Bovard PG, Heyroth FF: Roentgenographic changes and urinary fluoride excretion among workmen engaged in the manufacture of inorganic fluorides. Am J Roentgenol Radium Ther Nucl Med 65:42-48, 1951

39. Peperkorn, Kahling: [Osteopetrosis as consequence of a chronic fluorine intoxication.] Arbeitsschutz, Unfallverhutung Gewerbehygiene. Sonderausgabe des Reichsarbeitsblattes. Reichsarbeitsblatt Teil III No. 14/15:64-67, 1944 (Ger)

40. Dale PP, McCauley HB: Dental conditions in workers chronically exposed to dilute and anhydrous hydrofluoric acid. J Am Dent Assoc 37:131-40, 1948

41. McGarvey CJ, Ernstene AC: Skeletal changes in chronic fluorine intoxication--Report of a case. Cleve Clin Q 14:108-12, 1947

42. Largent EJ: The urinary fluoride excretion among men employed in alkylation plants using the hydrogen fluoride process. J Ind Hyg Toxicol 29:53-55, 1947

43. Collings GH Jr, Fleming RBL, May R: Absorption and excretion of inhaled fluorides. Arch Ind Hyg Occup Med 4:585-90, 1951

44. Collings GH Jr, Fleming RBL, May R, Bianconi WO: Absorption and excretion of inhaled fluorides--Further observations. Arch Ind Hyg Occup Med 6:368-73, 1952

45. Rye WA: Fluorides and phosphates--Clinical observations of employees in phosphate operation, in Proceedings of the 13th International Congress on Occupational Health, July 25-29, 1960, pp 361-64, 1961

46. Machle W, Evans EE: Exposure to fluorine in industry. J Ind Hyg Toxicol 22:213-17, 1940

47. Evans EE: An X-ray study of effects of industrial gases upon the human lung. Radiology 34:411-24, 1940

48. Derryberry OM, Bartholomew MD, Fleming RBL: Fluoride exposure and worker health--The health status of workers in a fertilizer manufacturing plant in relation to fluoride exposure. Arch Environ Health 6:503-14,1963

49. Leidel NA, Key MM, Henschel AF, Sutton GW, Haij ME, Willens N, Svalina J, Knudson JC, Jones HH, Kupel RE, Kinser RE, Mauer PL: Environmental and Medical Survey Blockson Works--Olin Mathieson Corporation, Joliet, Illinois. US Dept of Health, Education, and Welfare, Public Health Service, Bureau of Disease Prevention and Environmental Control, National Center for Urban and Industrial Health, Occupational Health Program, Sept 1967

50. Kaltreider NL, Elder MJ, Cralley LV, Colwell MO: Health survey of aluminum workers with special reference to fluoride exposure. J Occup Med 14:531-41, 1972

51. Johnson WH, Shuler PH, Curtis RA, Wallingford KM, Mangin HJ, Parnes W, Donaldson HM: Industrial Hygiene Survey, Ormet Corporation Aluminum Facilities, Hannibal, Ohio. Cincinnati, US Department Health, Education, and Welfare, National Institute for Occupational Safety and Health, Division of Field Studies and Clinical Investigations, March 15, 1973

52. Ronzani E: [Experimental studies on the effect of inhaling irritant industrial gases upon the organism's defense mechanisms against infectious diseases. (partial)] Arch Hyg 70:217-69, 1909 (Ger)

53. Machle W, Scott EW: The effects of the inhalation of hydrogen fluoride--III. Fluorine storage following exposure to sub-lethal concentrations. J Ind Hyg Toxicol 17:230-40, 1935

54. Machle W, Kitzmiller K: The effects of the inhalation of hydrogen fluoride--II. The response following exposure to low concentration. J Ind Hyg Toxicol 17:223-29, 1935

55. Stokinger HE: Toxicity following inhalation of fluorine and hydrogen fluoride, in Voegtlin C, Hodge HC (eds): Pharmacology and Toxicology of Uranium Compounds. New York, McGraw-Hill Book Company Inc, 1949, pp 1021-57

56. Smith FA, Gardner DE: A preliminary investigation of blood fluoride levels following exposure to hydrogen fluoride at a concentration of approximately 29 mg/m3, AECU-406. US Atomic Energy Commission, May 25, 1949, 20 pp

57. Stokinger HE, Ashenburg NJ, DeVoldre J, Scott JK, Smith FA: Acute inhalation toxicity of beryllium--II. The enhancing effect of the inhalation of hydrogen fluoride vapor on beryllium sulfate poisoning in animals. Arch Ind Hyg 1:398-410, 1950

58. Rosenholtz MJ, Carson TR, Weeks MH, Wilinski F, Ford DF, Oberst FW: A toxicopathologic study in animals after brief single exposures to hydrogen fluoride. Am Ind Hyg Assoc J 24:253-61, 1963

59. Higgins EA, Fiorca V, Thomas AA, Davis HV: Acute toxicity of brief exposures to HF, HCL, NO2, and HCN with and without CO. Fire Technol 8:120-30, 1972

60. Carney SA, Hall M, Lawrence JC, Ricketts CR: Rationale of the treatment of hydrofluoric acid burns. Br J Ind Med 31:317-21, 1974

61. Elfers LA, Decker CE: Determination of fluoride in air and stack gas samples by use of an ion specific electrode. Anal Chem 40:1658-61, 1968

62. Mandl RH, Weinstein LH, Weiskopf GJ, Major JL: The separation and collection of gaseous and particulate fluorides, in Englund HM, Beery WT (eds): Proceedings of the Second International Clean Air Congress. New York, Academic Press, 1971, pp 450-58

63. Panin KP: [Separate determination of inorganic fluorides, gaseous and in droplet aerosols, in air.] Gig Sanit 36:403-06, 1971 (Rus)

64. Habel K: The separation of gaseous and solid fluorine compounds during air-quality measurements. Staub-Reinhalt Luft 28:26-31, 1968

65. Dorsey JA, Kemnitz DA: A source sampling technique for particulate and gaseous fluorides. J Air Pollut Control Assoc 18:12-14, 1968

66. Jahr J: [A new dual filter method for separate determination of hydrogen fluoride and dustlike fluorides in the air.] Staub-Reinhalt Luft 32:17-22, 1972 (Ger)

67. Fluorides. Washington, DC, National Academy of Sciences, 1971

68. Pack MR, Hill AC, Thomas MD, Transtrum LG: Determination of gaseous and particulate inorganic fluorides in the atmosphere, in Symposium on Air Pollution Control, ASTM Special Technical Publication No 281. Baltimore, American Society for Testing Materials, 1960, pp 27-44

69. Mukai K, Ishida H: The alkaline filter paper method for surveying fluorides in the atmosphere. Paper No. A70-10 presented at American Institute of Mining, Metallurgy and Petroleum Engineers, Denver, Colorado, Feb 16-18, 1970.

70. Levaggi DA, Oyung W, Feldstein M: A comparative study of the determination of fluoride on lime paper by a colorimetric method and specific ion electrode method. Presented at the 10th State Health Department Methods Conference, San Francisco, Cal, Feb 19-21, 1969

71. Robinson E: Determining fluoride air concentrations by exposing limed filter paper. Am Ind Hyg Assoc Q 18:145-48, 1957

72. Adams DF: A quantitative study of the limed filter paper technique for fluorine air pollution studies. Int J Air Water Poll 4:247-55, 1961

73. Wilson WL, Campbell MW, Eddy LD, Poppe WH: Calibration of limed filter paper for measuring short-term hydrogen fluoride dosages--The effect of temperature, humidity, windspeed, and dose. Am Ind Hyg Assoc J 28:254-59, 1967

74. Pack MR, Hill AC: Further evaluation of glass fiber filters for sampling hydrogen fluoride. J Air Pollut Control Assoc 15:166-67, 1965

75. Pack MR, Hill AC, Benedict HM: Sampling atmospheric fluorides with glass fiber filters. J Air Pollut Control Assoc 13:374-77, 1963

76. Bourbon P: Analytical problems posed by pollution by fluorine compounds. J Air Pollut Control Assoc 17:661-63, 1967

77. Hydrogen Fluoride, NIOSH Method No. S176. Joint NIOSH-OSHA Standards Completion Program. US Dept of Health, Education and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, 1975, pp 1-7

78. Willard HH, Winter OB: Volumetric method for determination of fluorine. Ind Eng Chem (Anal Ed) 5:7-10, 1933

79. Weber SJ: Specific ion electrodes in pollution control. Am Lab 2:15-18, 20-23, 1973

80. Talvitie NA: Colorimetric determination of fluoride in natural waters with thorium and alizarin. Ind Eng Chem (Anal Ed) 15:620-21, 1943

81. Armstrong WD: Modification of the Willard-Winter method for fluorine determination. J Am Chem Soc 55:1741-42, 1933

82. McClure FJ: Microdetermination of fluorine by thorium nitrate titration. Ind Eng Chem (Anal Ed) 11:171-73, 1939

83. Smith FA, Gardner DE: A comparison of the thorium nitrate back-titration and the salt-acid thorium titration for the determination of fluoride. Arch Biochem 29:311-14, 1950

84. Nielsen JP, Dangerfield BS: Use of ion exchange resins for determination of atmospheric fluorides. Arch Ind Health 11:61-65, 1955

85. McKenna FE: Methods of fluorine and fluoride analysis--III. Nucleonics 9:51-58, 1951

86. McKenna FE: Methods of fluorine and fluoride analysis--I. Nucleonics 8:24-33, 1951

87. McKenna FE: Methods of fluorine and fluoride analysis--II. Nucleonics 9:40-49, 1951

88. Intersociety Committee (LV Cralley, chmn, Subcommittee 2): Tentative method of analysis for fluoride content of the atmosphere and plant tissues (manual methods) in Methods of Air Sampling and Analysis. Washington, DC, APHA, 1972, pp 246-65

89. Linde HW: Estimation of small amounts of fluoride in body fluids. Anal Chem 31:2092-94, 1959

90. Rao DN, Venkateswarlu P: Colorimetric estimation of fluorine in natural waters--Thorium-alizarin method improved. Indian J Med Res 39:223-27, 1951

91. Smith FA, Gardner DE: The determination of fluoride in urine. Am Ind Hyg Assoc Q 16:215-20, 1955

92. Megregian S, Maier FJ: Modified Zirconium-Alizarin reagent for determination of fluoride in water. J Amer Water Works Assoc 44:239-48, 1952

93. Megregian S: Rapid spectrophotometric determination of fluoride with Zirconium-Eriochrome Cyanine-R Lake. Anal Chem 26:1161-66, 1954

94. Adams DF, Koppe RK, Matzek NE: Colorimetric method for continuous recording analysis of atmospheric fluoride--Test chamber and interference studies with the mini-Adak analyzer. Anal Chem 33:117-19, 1961

95. Marshall BS, Wood R: A simple field test for the determination of hydrogen fluoride in air. Analyst 93:821-26, 1968

96. Mulder GJ: [The microdetermination of fluoride in urine.] Weekbl 94:329-45, 1959 (Nor)

97. Sarma PL: Spectrophotometric determination of fluoride by Zirconium-Eriochrome Cyanine-R. Anal Chem 36:1684-85, 1964

98. Belcher R, West TS: A study of the cerium III-Alizarin complexan-fluoride reaction. Talanta 8:853-62, 1961

99. Derner HA: Semiautomated determination of fluoride in urine. Am Ind Hyg Assoc 28:357-62, 1967

100. West PW, Lyles GR, Miller JL: Spectrophotometric determination of atmospheric fluorides. Environ Sci Technol 4:487-91, 1970

101. Weinstein LH, Mandl RH, McCune DC, Jacobson JS, Hitchcock AE: Semi-automated analysis of fluoride in biological materials. J Air Pollut Control Assoc 15:222-25, 1965

102. Waldo AL, Zipf RE: The determination of fluoride in drinking water and biological materials. J Lab Clin Med 40:601-09, 1952

103. Schenk GH, Dilloway KP: Determination of fluoride by fluorescence quenching. Anal Let 2:379-85, 1969

104. Ivanov T, Koen E: [Improved method for determination of HF applied in the sanitary-chemical control of working environment.] Khig Zdraveopaz 9:80-84, 1956 (Bul)

105. Bellack E, Schouboe PJ: Rapid photometric determination of fluoride in water--Use of sodium 2-(p-sulfophenylazo)-1, 8-dihydroxynaphthalene-3, 6-disulfonate-Zirconium Lake. Anal Chem 30:2032-34, 1958

106. Marier JR, Rose D: The fluoride content of some foods and beverages--A brief survey using a modified Zr-SPADNS method. J Food Sci 31:941-46, 1966

107. Abernethy RF, Gibson FH: Method for determination of fluorine in coal, report of investigations 7054. US Dept of Interior, Bureau of Mines, 1967, p 13

108. Macejunas AG: Spectrophotometric determination of fluoride using Zirconium-Xylenol orange. J Amer Water Works Assoc 61:311-13, 1969

109. Demidov AV, Mokhov LA: Rapid methods for the determination of inorganic substances in the air, in USSR Literature on Air Pollution

and Related Occupational Diseases--A Survey. US Dept Health, Education, and Welfare, Public Health Service, 1964, vol 10, pp 60-61

110. Ivie JO, Zielenski LF, Thomas MD, Thompson CR: Atmospheric fluorometric fluoride analyzer. J Air Pollut Control Assoc 15:195-97, 1965

111. Dubois L, Monkman JL, Teichman T: The determination of urinary fluorides. Am Ind Hyg Assoc J 23:157-63, 1962

112. Kojima T, Mitsunojo I, Seo Y: Selective gas-chromatographic detection using an ion-selective electrode--II. Selective detection of fluorine compounds. Talanta 19:539-47, 1972

113. Fresen JA, Cox FH, Witter MJ: The determination of fluoride in biological materials by means of gas chromatography. Pharm Weekbl 103:909-14, 1968

114. Cropper E, Puttnam NA: The gas chromatographic determination of fluoride in dental creams. J Soc Cosmetic Chem 21:533-40, 1970

115. Gutsche B, Herrmann R, Rudiger K: [A fluorine-specific detector for gas chromatography.] Z Anal Chem 258:273-77, 1975 (Ger)

116. Gutsche B, Herrmann R: [Simplified fluorine-specific detector for gas chromatography.] Z Anal Chem: 259:126-27, 1972 (Ger)

117. Lennox D, Leroux J: Applications of X-ray diffraction analysis in the environmental field. Arch Ind Hyg 8:359-70, 1953

118. Spoonemore JW: A Method of Determining Trace Amounts of Fluorine in Lithium-Fluoride Samples by Means of Neutron Activation Analysis, MS thesis. Seattle, University of Washington, 1963

119. Bond AM, O'Donnell TA: Determination of fluoride by atomic absorption spectrometry. Anal Chem 40:560-63, 1968

120. Bresler PI: [Photometric determination of fluorine and hydrogen fluoride in gas mixtures.] Zh Anal Khim 27:145-50, 1972 (Rus)

121. Kakabadse GJ, Manohin B, Bather JM, Weller EC, Woodbridge P: Decomposition and the determination of fluorine in biological materials. Nature 229:626-27, 1971

122. van Leuven HCE: Organic multi-element analysis with a small mass spectrometer as detector--A preliminary note. Anal Chim Acta 49:364-66, 1970

123. Adams DF: An automatic hydrogen fluoride recorder proposed for industrial hygiene and stack monitoring. Anal Chem 32:1312-16, 1960

124. Mavrodineanu R, Coe RR: Improved apparatus and procedures for sampling and analyzing air for fluorides. Contrib Boyce Thompson Inst 18:173-80, 1955

125. Cumpston AG, Dinman BD: A modified diffusion method for the determination of urinary fluoride. Am Ind Hyg Assoc J 26:461-64, 1965

126. Bien SM: A new micro-method for the determination of fluorides. J Dent Res 22:123-27, 1943

127. Howard OH, Weber CW: An improved continuous internal-electrolysis analyzer for gaseous fluorides in industrial environments. Am Ind Hyg Assoc J 23:48-57, 1962

128. Jacobson JS, McCune DC, Weinstein LH, Mandl RH, Hitchcock AE: Studies on the measurement of fluoride in air and plant tissues by the Willard-Winter and semiautomated methods. J Air Pollut Control Assoc 16:367-71, 1966

129. Howard OH, Weber CW: A portable continuous analyzer for gaseous fluorides in industrial environments. Arch Ind Health 19:355-64, 1959

130. Nichols PNR: The simple modification of a commercial sulphur dioxide meter for the determination of the atmospheric pollutants. Chem Ind 39:1654-55, 1964

131. Thompson CR, Zielenski LF, Ivie JO: A simplified fluorometric fluoride analyzer. Atmos Environ 1:253-59, 1967

132. Ke PJ, Regier LW, Power HE: Determination of fluoride in biological samples by a nonfusion distillation and ion-selective membrane electrode method. Anal Chem 41:1081-84, 1969

133. Byczkowski S, Krechniak J, Gietazyn T: An attempt to evaluate exposure to fluorides based upon fluoride levels in hair. Fluoride 4:98-100, 1971

134. Health of Workers Exposed to Sodium Fluoride at Open Hearth Furnaces, PHS bulletin No. 299. Federal Security Agency, Public Health Service, 1948, 64 pp

135. Harwood JE: The use of an ion-selective electrode for routine fluoride analyses on water samples. Water Res 3:273-80, 1969

136. Singer L, Armstrong WD: Determination of fluoride procedure based upon diffusion of hydrogen fluoride. Anal Biochem 10: 495-500, 1965

137. Murray MM, Ryle JA, Simpson BW, Wilson DC: Thyroid enlargement and other changes related to the mineral content of drinking water (with

a note on goitre prophylaxis). Medical Research Council Memorandum, No. 18, London, His Majesty's Stationery Office, 1948, p 28

138. Neefus JD, Cholak J, Saltzman BE: The determination of fluoride in urine using a fluoride-specific ion electrode. Am Ind Hyg Assoc J 31:96-99, 1970

139. Sun M: Fluoride ion activity electrode for determination of urinary fluoride. Am Ind Hyg Assoc J 30:133-36, 1969

140. Singer L, Armstrong WD, Vogel JJ: Determination of fluoride content of urine by electrode potential measurements. J Lab Clin Med 74:354-58, 1969

141. Rausa G, Trivello R: A spectrophotometric method for detecting fluorine in urine. Ig Mod 63:89-103, 1970 (Ita)

142. McHenry CR, Hoyt C: Monitoring of fluoride content of air, water, and vegetation. J Air Pollut Control Assoc 11:66-70, 1961

143. MacLeod KE, Crist HL: Comparison of the SPADNS-Zirconium Lake and specific ion electrode methods of fluoride determination in stack emission samples. Anal Chem 45:1272-73, 1973

144. Cernik AA, Cooke JA, Hall RJ: Specific ion electrode in the determination of urinary fluoride. Nature 227:1260-61, 1970

145. Liberti A, Mascini M: Determination of fluorides in polluted air by use of an ion specific electrode. Fluoride Q 4:49-56, 1971

146. Liberti A, Mascini M: Anion determination with ion selective electrodes using Gran's plots--Application to fluoride. Anal Chem 41:676-79, 1969

147. Harzdorf C: [Use of a fluoride-specific electrode in automatic potentiometric titrations.] Z Anal Chem 245:67-70, 1969 (Ger)

148. Standard Methods of Test for Fluoride Ion in Water, in ASTM Standards. Industrial Water--Atmospheric Analyses Pt 23, 1972. ASTM Designation--D1179-72, pp 191-96

149. Boddey RF: The use of chemicals in the modern foundry. Ann Occup Hyg 10:231-39, 1967

150. Poppe WH: The potential fluorine hazard in the fertilizer industry. Commer Fert 88:42-45, 73, 76, 1954

151. Tebbens BD, Drinker P: Ventilation in arc welding with coated electrodes. J Ind Hyg Toxicol 23:322-42, 1941

152. Jones RC: Selective tests for contaminants in welding fumes from electric arc welding--An environmental assessment. Ann Occup Hyg 10:369-73, 1967

153. Drinker P, Nelson KW: Welding fumes in steel fabrication. Ind Med 13:673-75, 1944

154. Thrysin E, Gerhardsson G, Forssman S: Fumes and gases in arc welding. Arch Ind Hyg 6:381-403, 1952

155. Krechniak J: Fluoride hazards among welders. Fluoride Q Rep 2:13-24, 1969

156. Feiner B, Moskowitz S: Health hazards in manufacture of quartz crystals used in radio communications. NY State Ind Bull 23:105-06, 1944

157. Scott AM: Health hazards in the production of printed wiring. Trans Inst Met Finish 45:102-06, 1967

158. Dickson DB, Paganini O: Health hazards in the manufacture of neon signs. Am Ind Hyg Assoc Q 12:25-29, 1951

159. Laskin S, Turner RAN, Stokinger HE: An analysis of dust and fume hazards in a beryllium plant, in Vorwald AJ (ed): Pneumoconiosis--Beryllium, Bauxite Fumes, Compensation. New York, Paul B Hoeber, Inc, 1950, pp 360-86

160. Jager LE: Hazards in the plating industry. Mich Occup Health 11:2-8, Winter 1965-66

161. Arnest RT: Atmosphere control in closed space environment (submarine). US Naval Medical Research Laboratory Report No. 367. New London, Conn. Bureau of Medicine and Surgery, Dec 14, 1961, AD 270 896

162. Salls CM: Hydrofluoric acid fumes. Ind Hyg Bull 1:10-11, 1924

163. Bowditch M, Drinker CK, Drinker P, Haggard HH, Hamilton A: Code for safe concentrations of certain common toxic substances used in industry. J Ind Hyg Toxicol 22:251, 1940

164. Cook WA: Maximum allowable concentrations of industrial atmospheric contaminants. Ind Med 14:936-46, 1945

165. Bloomfield JJ: Codes for the prevention and control of occupational diseases. Ind Hyg Found Bull 8:71-79, 1947

166. 1947 MAC values. Ind Hyg Newsletter 7:15-16, 1947

167. Threshold Limit Values Adopted at April 1948 Meeting of American Conference of Governmental Industrial Hygienists in Boston, Massachusetts. Cincinnati, American Conference of Governmental Industrial Hygienists, 1948

168. American Conference of Governmental Industrial Hygienists, Committee on Threshold Limit Values: Documentation of the Threshold Limit Values. Cincinnati, ACGIH, 1962, pp 56-57

169. American Conference of Governmental Industrial Hygienists, Committee on Threshold Limit Values: Documentation of the Threshold Limit Values, ed 2. Cincinnati, ACGIH, 1966, p 104

170. American Conference of Governmental Industrial Hygienists, Committee on Threshold Limit Values: Documentation of the Threshold Limit Values for Substances in Workroom Air, ed 3. Cincinnati, ACGIH, 1971, p 31

171. Heyroth FF: The Halogens, in Patty FA: Industrial Hygiene and Toxicology, New York, Interscience Publishers Inc, 1949, vol 2, pp 542-44

172. Largent EJ: The metabolism of fluorides in man. Arch Ind Health 21:318-23, 1960

173. United States of America Standards Institute: Acceptable Concentrations of Hydrogen Fluoride and Inorganic Fluoride Dusts, Z:37.28-1966. New York, United States of America Standards Institute, 1966, pp 7-12

174. Heyroth FF: Halogens, in Patty FA (ed): Industrial Hygiene and Toxicology, ed 1 rev; Toxicology (Fassett DW, Irish DD, eds). New York, Interscience Publishers Inc, 1963, vol 2, pp 832-44

175. Pennsylvania Dept of Environmental Resources: Title 25: Rules and Regulations; Pt 1: Dept of Environmental Resources; Subpart D: Environmental Health and Safety; Article IV: Occupational Health and Safety; Chapter 201: Places of Employment; Subchapter A: Threshold Limits. 201.1-201.121 Adopted Sept 28, 1971, effective Nov 1, 1971

176. Short Term Limits for Exposure to Airborne Contaminants--A Documentation. Harrisburg, Pennsylvania Dept of Health, Div of Occupational Health [n.d.]

177. Czechoslovak Committee of MAC: Documentation of MAC in Czechoslovakia. Prague, June 1969, pp 93-95

178. [Documentation of permissible concentrations of hazardous substances in working environment (basis of proposal)--1971.] Sangyo Igaku 14:45-90, 1972 (Jap)

179. Permissible Levels of Toxic Substances in the Working Environment. Occupational Safety and Health Series No. 20. Geneva, International Labour Office, 1970, pp 190, 202

180. WHO Committee on Occupational Health: Permissible levels of toxic substances in the working environment, Occupational Safety and Health Series 20. Geneva, International Labour Office, 1970

181. Threshold Limit Values for 1973, Technical Data Note 2/73. Dept of Employment, HM Factory Inspectorate

182. Yanin LV (ed): Permissible concentrations of toxic gases, vapors and dust in the air of work premises, in Labor Hygiene and Industrial Sanitation. Gosudarstvennoe Izdatell stvo Meditsinski Literatury. Moskva, 1962, Part 1, pp 207-12

183. [Recommendation for permissible concentrations, etc.] Sangyo Igaku 13:475-84, 1971 (Jap)

184. Stevenson CA, Watson AR: Fluoride osteosclerosis. Am J Roentgenol Radium Ther Nucl Med 78: 13-18, 1957

185. Elkins HB, Pagnotto LD, Smith HL: Concentration adjustments in urinalysis. Am Ind Hyg Assoc J 35:559-65, 1974

186. Boice JD, Burnett BM: Considerations of possible pregnancy in the use of diagnostic X-rays, in Health Physics in the Healing Arts, 7th Midyear Topical Symposium FDA 73-8029

187. Fanciullini H: Preventing the danger of burns when using hydrofluoric acid. World Congress on the Prevention of Occupational Risks, 3d. Paris, 1961, pp 430-33

188. Baxter HG: The design, operation and hazards of a detergent alkylate plant. Ann Occup Hyg 14:137-43, 1971

189. Hydrofluoric acid (aqueous), National Safety Council Data Sheet 459. Chicago, National Safety Council, 1957

190. Inorganic fluorides, National Safety Council Data Sheet 442. Chicago, National Safety Council, 1957

191. Benson R: Hydrogen fluoride exposure--Prevention, in the operation of HF alkylation plants. Ind Med 13:113-17, 1944

192. Fehr CM: How to handle anhydrous hydrofluoric acid safely. Pet Refiner 22:239-44, 1943

193. Flowers TE: The safe handling of hydrofluoric acid in a petroleum refinery. Proceedings of the American Petroleum Institute, Section 28(Sec I):95-98, 1948

194. Fehr CM: The safe handling and storage of anhydrous hydrofluoric acid. Chem Ind 43:505-10, 1943

195. Crowe WH, Marysiuk AM: Working safely with HF alkylation. Proceedings of the American Petroleum Institute 45:113-20, 1965

196. Potter AL: Protective measures in the chemical industry. Trans Assoc Ind Med Off 6:32-36, Apr 1956

197. Chlorine and fluorine hazards. Chem Age (London), pp 1315-16, June 16, 1956

198. Hydrofluoric acid (anhydrous or aqueous). MCA Chem-Card--Transportation Emergency Guide CC-42. Washington, DC, Manufacturing Chemists' Association Inc, August 1965

199. Meyer WR: Hazards in the plating room. Technical Proceedings of the 47th Annual Convention of the American Electroplaters' Society, 47:55-58, 1960

200. Guthrie VB: How to handle chemicals safely--API medical group prepares data reports on 31 more toxic materials--Review now total 63. Pet Process, 9:1203-04, 1954

201. American Conference of Governmental Industrial Hygienists Committee on Industrial Ventilation: Industrial Ventilation--A Manual of Recommended Practice, ed 14. Lansing, ACGIH, 1975

202. Gafafer WM: Occupational Diseases--A Guide to Their Recognition, Public Health Service bulletin No. 1097. US Dept of Health, Education, and Welfare, 1964, pp 148-50

203. Crowe WH, Marysiuk AM: How to work safely with HF alkylation. Hydrocarbon Process Pet Refiner 44:192-94, 1965

204. Basic Elements of Respiratory Protection. Pittsburgh, Mine Safety Appliances Co, 1972, 20 pp

205. Hydrogen fluoride. Cargo Information Card CIC-54. Washington, DC, Manufacturing Chemists' Association Inc, May 1970

206. Hydrofluoric acid. Cargo Information Card CIC-52. Washington, DC, Manufacturing Chemists' Association Inc, May 1970

207. Ziehlke KT, Petit GS, Kimmerly EY, Weber CW: Hydrogen Fluoride Cylinder Failure. Oak Ridge, Tennessee Gaseous Diffusion Plant, Union Carbide Corporation, Nuclear Division, Sept 16, 1969

208. Whitaker GC: Corrosion of metals in fluorine and hydrofluoric acid. Corrosion 6:283-85, 1950

209. Davis WL: Ambient air fluorides in Salt Lake County. Rocky Mt Med J 69:53-56, 1972

210. Pennsylvania Dept of Environmental Resources: Title 25: Rules and Regulations; Pt I: Dept of Environmental Resources; Subpart C: Protection of Natural Resources; Article III: Air Resources; Chapter 131: Ambient Air Quality Standards. 131.1-131.4. Adopted Sept 2, 1971, rev Jan 27, 1972

211. Weaver NK: Atmospheric contaminants and standards--Status report. J Occup Med 11:445-61, 1969

212. Washington Administrative Code 18-48 (4-1-71)

213. Inorganic fluorides. Air Quality Guide No 13. New York (State) Dept of Environmental Conservation, Div of Air Resources, Aug 1972

214. Inorganic Fluorides. Am Ind Hyg Assoc J 30:98-101, 1969

215. National Institute for Occupational Safety and Health, Division of Laboratories and Criteria Development: Fluoride in Urine--Physical and Chemical Analysis Branch Method 114, in NIOSH Manual of Analytical Methods, HEW publication No. (NIOSH) 75-121. Cincinnati, US Dept of Health, Education, and Welfare, Public Health Service, Center for Disease Control, NIOSH, 1974, pp 114-1 to 114-5

IX. APPENDIX I

AIR SAMPLING PRACTICES FOR HYDROGEN FLUORIDE

General Requirements

Concentrations of HF in the air shall be determined within the worker's breathing zone and shall meet the following criteria in order to evaluate conformance with the standard:

(a) Samples collected shall be representative of the individual worker's exposure.

(b) Sample data sheets shall include:

- (1) The date and time of sample collection.
- (2) Sampling duration.
- (3) Volumetric flowrate of sampling.
- (4) A description of the sampling location.
- (5) Ambient temperature and pressure.
- (6) Other pertinent information (eg, worker's name, shift, work process).

(c) Sampling will be in accordance with the provisions of the procedures outlined herein.

Breathing Zone Sampling

In order to assure that a sample is representative of a worker's exposure, collection shall be as near the breathing zone of the worker as practical. Sampling should not hamper the typical movements associated with his work, but care should be taken that the bubbler is maintained in a vertical position during sampling.

A portable, battery-operated, personal sampling pump capable of being calibrated to ±5% at the required flow and a standard glass midget bubbler containing 0.1 N sodium hydroxide solution shall be used to collect the sample (see Figure XII-1). The bubbler solution is prepared by dissolving 4 g of sodium hydroxide in 1 liter of distilled water.

The sampling rate shall be accurately determined and maintained at a value of approximately 1.5 liters/minute; each sample taken to determine a TWA concentration shall be collected for 30 minutes.

The minimum number of TWA exposure determinations for an operation or process shall be based on the number of workers exposed as provided in Table I-2. The TWA may be determined as follows:

$$\text{TWA} = \frac{C1t1 + C2t2 + \ldots + Cntn}{T}$$

where: C = HF or HF acid concentration (C1,C2,C3...Cn) during any sampling period t1,t2,t3...tn, respectively.
T = the sum of all sampling periods (t1,2,3...n)

Samples, taken to determine if airborne HF concentrations greater than the ceiling concentration exist, shall be collected at a rate of 1.5 liters/minute for 15 minutes.

A "blank" bubbler should be handled in the same manner as the bubblers containing the samples (fill, seal, and transport) except that no air is sampled through this bubbler.

Calibration of Sampling Trains

Since the accuracy of an analysis can be no better than the accuracy of the volume of air which is measured, the accurate calibration of a sampling pump is essential to the correct interpretation of the volume indicator. The frequency of calibration is dependent on the use, care, and handling to which the pump is subjected. In addition, pumps should be recalibrated if they have been subjected to misuse, or if they have just been repaired or received from a manufacturer. If the pump receives hard usage, more frequent calibration may be necessary. Ordinarily, pumps should be calibrated in the laboratory both before they are used in the field, and after they have been used to collect a large number of field samples.

The accuracy of calibration is dependent on the type of instrument used as a reference. The choice of calibration instrument will depend largely upon where the calibration is to be performed. For laboratory testing, a 1- or 2-liter buret or a wet-test meter is recommended, although other standard calibrating instruments such as a spirometer or dry gas meter can be used.

Instructions for calibration with the soapbubble flow meter follow. However, if an alternative calibration device is selected, equivalent procedures should be used. The calibration setup for personal sampling pumps with a midget bubbler is shown in Figure XII-1.

(a) Check the voltage of the pump battery with a voltmeter both with the pump off and while it is operating to assure adequate voltage for calibration. If necessary, charge the battery to the manufacturer's specifications.

(b) Fill the bubbler with 10 ml of the absorbing solution.

(c) Assemble the sampling train as shown in Figure XII-1.

(d) Turn the pump on and moisten the inside of the soapbubble meter by immersing the buret in the soap solution and drawing bubbles up the inside of the buret until they are able to travel the entire buret length without bursting.

(e) Adjust the pump rotameter to provide a flowrate of 1.5 liters/minute.

(f) Check the water manometer to ensure that the pressure drop across the sampling train does not exceed 13 inches of water (approximately 1 inch of mercury).

(g) Start a soapbubble up the buret and, with a stopwatch, measure the time it takes for the bubble to transit a minimum of 1.0 liter.

(h) Repeat the procedure in (g) above at least three times, average the results, and calculate the flowrate by dividing the volume between the preselected marks by the time required for the soap bubble to travel the distance.

(i) Data for the calibration include the volume measured, elapsed time, pressure drop, air temperature, atmospheric pressure, serial number of the pump, date, and name of the person performing the calibration.

(j) Corrections to the flowrate may be necessary if the pressure or temperature when samples are collected differs significantly from that when calibration was performed. Flow rates may be calculcated by using the following formula:

$$q\ (\text{actual}) = q\ (\text{indicated}) \times \frac{P\ (\text{calibrated})}{P\ (\text{actual})} \times \frac{T\ (\text{actual})}{T\ (\text{calibrated})}$$

where:

q = volumetric flowrate

P = pressure

T = temperature (Kelvin or Rankine)

(k) Use graph paper to record the air flow corrected to 25 C and 760 mmHg as the ordinate and the rotameter readings as the abscissa.

X. APPENDIX II

ANALYTICAL METHOD FOR HYDROGEN FLUORIDE

Principle of the Method [77]

A known volume of air is drawn through a midget bubbler containing 10 ml of 0.1 N sodium hydroxide to trap hydrogen fluoride. The resulting solution is diluted to 25 ml with 0.1 N sodium hydroxide and buffered with an equal volume of total ionic strength activity buffer (TISAB). If a urine sample is involved, equal volumes of urine and TISAB are mixed. The sample is analyzed using a fluoride ion-selective electrode and an expanded scale millivoltmeter.

Range and Sensitivity

This method was validated over the range of 1.329-4.50 mg/cu m at an airborne temperature of 22 C and pressure of 761 mmHg using a 45-liter sample. The probable useful range of this method is 0.245-7.35 mg/cu m for 45-liter samples.

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/minute from a test atmosphere containing 4.50 mg/cu m.

Interferences

Hydroxide ion is the only significant electrode interference, however, addition of the TISAB minimizes this problem. Very large amounts of complexing metal ions such as aluminum may result in low readings even in the presence of TISAB.

When contaminants other than fluorides are known or suspected to be present in the air during sampling, such information should be transmitted with the sample.

Precision and Accuracy

The Coefficient of Variation (CVT) for the total analytical and sampling method in the range of 1.329-4.50 mg/cu m was 0.057. This value corresponds to a standard deviation of 0.14 mg/cu m at the recommended environmental limit.

A collection efficiency of 0.991 ± 0.004 was determined for the collecting medium.

Apparatus

The sampling unit for the bubbler collection method consists of the following components:

(a) A standard glass midget bubbler containing the absorption medium. The bubbler stem unit consists of a 2-hole rubber stopper to fit 1/8-in OD Teflon tubing.

(b) A pump suitable for pumping at least 1.5 liters air/minute for 30 minutes. The sampling pump must be protected from splashover or solvent condensation by a 5-cm long by 6-mm ID glass tube loosely packed with a plug of glass wool and inserted between the exit arm of the bubbler and the pump.

(c) Thermometer.

(d) Manometer.

(e) Volumetric flasks: 25-ml or convenient sizes.

(f) Pipets: 1-, 2-, 4-, and 5-ml.

(g) Fluoride ion-selective electrode.

(h) Reference electrode, single junction, calomel or silver/ silver chloride electrode.

(i) Expanded scale millivolt-pH meter capable of measuring to within 0.5 millivolt.

(j) Polyethylene beakers, 50-ml capacity.

(k) Magnetic stirrer with heat shield between stirring motor and sample, and stirring bars for 50-ml beakers.

(l) Stopwatch.

(m) Laboratory oven, thermostatically controlled.

All glassware and plastic ware should be washed in detergent solution, rinsed in tap water, and then rinsed with doubly distilled water.

All sampling devices, volumetric glassware, and reagent solutions must be stored under suitable conditions to protect from airborne dust and fumes, and should be reserved for exclusive use in low-fluoride analyses.

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.

(a) Doubly distilled water.

(b) Glacial acetic acid.

(c) Sodium hydroxide, 5 N solution. Dissolve 28 g of sodium hydroxide in sufficient distilled water to give 300 ml of solution.

(d) Sodium chloride.

(e) Sodium citrate.

(f) 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 5.0. Cool to room temperature and pour into a 1-liter volumetric flask and add doubly distilled water to the mark.

(g) Ethylenedinitrilotetracetic acid (EDTA), disodium salt.

(h) Sodium fluoride, for preparation of standards.

(i) Standard fluoride solution.

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 fluoride ion. One ml of this solution contains the amount collected at 0.5 times the recommended environmental limit when sampling at 1.5 liters/minute for 30 minutes. The 0.5X level standard solution is made by combining 10 ml of

0.1 N sodium hydroxide with 1 ml of the standard stock solution. Likewise, the 1X level standard solution is prepared with 2 ml, and the 2X level standard solution 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-selective electrode.

Collection of Samples

Pour 10 ml of the collection medium into the midget bubbler, using a graduated cylinder to measure the volume.

Connect the bubbler (via the adsorption tube) to the vacuum pump with a short piece of flexible tubing. The air being sampled should not pass through any other tubing or other equipment before entering the bubbler.

The bubbler stem unit consists of a 2-hole rubber stopper to fit 1/8-in OD Teflon tubing. One piece of tubing conducts the analyte to below the level of the collection medium where the analyte is trapped. The short outlet tube is connected to the sampling pump.

Turn the pump on to begin sample collection. Care must be taken to measure the flow rate and time 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/minute. The flowrate should be known with an accuracy of ±5%.

The pump rotameter should be observed frequently and adjusted if necessary, and sampling should be terminated at any evidence of a problem.

Terminate sampling at the predetermined time and note sample flow rate and collection time.

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.

Care should be taken to minimize spillage or loss by evaporation at all times. Refrigerate samples if analysis cannot be done within a day.

Calibration and Standards

Prepare three fluoride standard solutions as described under Reagents at each of three levels (0.5X, 1X, and 2X the recommended workplace environmental limit).

Insert the fluoride ion-selective electrode and the reference electrode into one of the standards at the 0.5X level, and stir the solution with the magnetic stirrer.

Record the resulting millivolt reading to the nearest 0.5 millivolt.

Repeat the above two steps for the remaining standard solutions.

Calibration at each level should be repeated twice daily.

Average the millivolt readings at each level.

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.

Analysis of Samples

The sample in each bubbler is analyzed separately.

Quantitatively transfer the contents of the polyethylene bottle to a 25-ml volumetric flask. Make up to volume with 0.1 N sodium hydroxide.

Transfer the sample to a 50-ml polyethylene beaker. Add 25 ml of TISAB and stir with a magnetic stirrer.

Lower the fluoride ion-selective electrode and reference electrode into the stirred solution and record the resulting millivolt reading (to the nearest 0.5 mV) after it has stabilized to a drift rate of less than 0.5 mV/min.

Urine Samples

Urine samples should be collected in chemically clean bottles containing 0.2 g of EDTA. If the volume of the urine sample as determined upon receipt is greater than 100 ml, an amount of EDTA equivalent to 0.2 g/100 ml in excess of the first 100 ml should be added. Care must be taken when collecting and handling urine specimens to avoid F contamination. Upon receipt of the sample, either analyze immediately or refrigerate to retard bacterial action on urea which increases the sample pH through the generation of ammonia. Determine the specific gravity before analysis. Transfer 10 ml of well-mixed urine sample and 10 ml of TISAB into a 50-ml plastic beaker and stir with a magnetic stirrer. Proceed directly with electrode analysis. Determine F concentration by referring to a previously prepared standard curve. Calculate to mean specific gravity of 1.024. If a urinometer is used which has been calibrated against water at 4 C, a temperature correction must be made. [215]

Calculations

Read the weight in milligrams 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.

Corrections for the blank must be made for each sample.

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

where:

mg sample = mg F found in sample bubbler

mg blank = mg F found in blank bubbler

Calculate the mg of hydrogen fluoride found by multiplying the mg of fluoride ion found (corrected value) by 1.05.

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

$$\text{mg/cu m} = \frac{\text{Corrected mg X 1000 liter/cu m}}{\text{Air volume sampled (liter)}}$$

Another method of expressing concentration is ppm.

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

where:

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

XI. APPENDIX III

MATERIAL SAFETY DATA SHEET

The following items of information which are applicable to a specific product or material shall be provided in the appropriate block of the Material Safety Data Sheet (MSDS).

The product designation is inserted in the block in the upper left corner of the first page to facilitate filing and retrieval. Print in upper case letters as large as possible. It should be printed to read upright with the sheet turned sideways. The product designation is that name or code designation which appears on the label, or by which the product is sold or known by employees. The relative numerical hazard ratings and key statements are those determined by the rules in Chapter V, Part B, of the NIOSH publication, An Identification System for Occupationally Hazardous Materials. The company identification may be printed in the upper right corner if desired.

(a) Section I. Product Identification

The manufacturer's name, address, and regular and emergency telephone numbers (including area code) are inserted in the appropriate blocks of Section I. The company listed should be a source of detailed backup information on the hazards of the material(s) covered by the MSDS. The listing of suppliers or wholesale distributors is discouraged. The trade name should be the product designation or common name associated with the material. The synonyms are those commonly used for the product, especially formal chemical nomenclature. Every known chemical designation or competitor's trade name need not be listed.

(b) Section II. Hazardous Ingredients

The "materials" listed in Section II shall be those substances which are part of the hazardous product covered by the MSDS and individually meet any of the criteria defining a hazardous material. Thus, one component of a multicomponent product might be listed because of its toxicity, another component because of its flammability, while a third component could be included both for its toxicity and its reactivity. Note that a MSDS for a single component product must have the name of the material repeated in this section to avoid giving the impression that there are no hazardous ingredients.

Chemical substances should be listed according to their complete name derived from a recognized system of nomenclature. Where possible, avoid using common names and general class names such as "aromatic amine," "safety solvent," or "aliphatic hydrocarbon" when the specific name is known.

The "%" may be the approximate percentage by weight or volume (indicate basis) which each hazardous ingredient of the mixture bears to the whole mixture. This may be indicated as a range or maximum amount, ie, "10-40% vol" or "10% max wt" to avoid disclosure of trade secrets.

Toxic hazard data shall be stated in terms of concentration, mode of exposure or test, and animal used, ie, "100 ppm LC50-rat," "25 mg/kg LD50-skin-rabbit," "75 ppm LC man," or "permissible exposure from 29 CFR 1910.1000," or, if not available, from other sources of publications such as the American Conference of Governmental Industrial Hygienists or the American National Standards Institute Inc. Flammable or reactive data could be flash point, shock sensitivity, or other brief data indicating nature of the hazard.

(c) Section III. Physical Data

The data in Section III should be for the total mixture and should include the boiling point and melting point in degrees Fahrenheit (Celsius in parentheses); vapor pressure, in conventional millimeters of mercury (mmHg); vapor density of gas or vapor (air = 1); solubility in water, in parts/hundred parts of water by weight; specific gravity (water = 1); percent volatiles (indicated if by weight or volume) at 70 Fahrenheit (21.1 Celsius); evaporation rate for liquids or sublimable solids, relative to butyl acetate; and appearance and odor. These data are useful for the control of toxic substances. Boiling point, vapor density, percent volatiles, vapor pressure, and evaporation are useful for designing proper ventilation equipment. This information is also useful for design and deployment of adequate fire and spill containment equipment. The appearance and odor may facilitate identification of substances stored in improperly marked containers, or when spilled.

(d) Section IV. Fire and Explosion Data

Section IV should contain complete fire and explosion data for the product, including flash point and autoignition temperature in degrees Fahrenheit (Celsius in parentheses); flammable limits, in percent by volume in air; suitable extinguishing media or materials; special firefighting procedures; and unusual fire and explosion hazard information. If the product presents no fire hazard, insert "NO FIRE HAZARD" on the line labeled "Extinguishing Media."

(e) Section V. Health Hazard Information

The "health Hazard Data" should be a combined estimate of the hazard of the total product. This can be expressed as a TWA concentration, as a permissible exposure, or by some other indication of an acceptable standard. Other data are acceptable, such as lowest LD50, if multiple components are involved.

Under "Routes of Exposure," comments in each category should reflect the potential hazard from absorption by the route in question. Comments should indicate the severity of the effect and the basis for the statement if possible. The basis might be animal studies, analogy with similar products, or human experiences. Comments such as "yes" or "possible" are not helpful. Typical comments might be:

> Skin Contact--single short contact, development of painful burns; prolonged or repeated contact, extreme pain and tissue destruction.
>
> Eye Contact--intense pain and tissue destruction; corneal scarring.

"Emergency and First Aid Procedures" should be written in lay language and should primarily represent first aid treatment that could be provided by paramedical personnel or individuals trained in first aid.

Information in the "Notes to Physician" section should include any special medical information which would be of assistance to an attending physician including required or recommended preplacement and periodic medical examinations, diagnostic procedures, and medical management of overexposed workers.

(f) Section VI. Reactivity Data

The comments in Section VI relate to safe storage and handling of hazardous, unstable substances. It is particularly important to highlight instability or incompatibility to common substances or circumstances such as water, direct sunlight, steel or copper piping, acids, alkalies, etc. "Hazardous Decomposition Products" shall include those products released under fire conditions. It must also include dangerous products produced by aging, such as peroxides in the case of some ethers. Where applicable, shelf life should also be indicated.

(g) Section VII. Spill or Leak Procedures

Detailed procedures for cleanup and disposal should be listed with emphasis on precautions to be taken to protect workers assigned to cleanup detail. Specific neutralizing chemicals or procedures should be described in detail. Disposal methods should be explicit including proper labeling of containers holding residues and ultimate disposal methods such as "sanitary landfill," or "incineration." Warnings such as "comply with local, state, and federal antipollution ordinances" are proper but not sufficient. Pertinent specific local requirements shall be identified.

(h) Section VIII. Special Protection Information

Section VIII requires specific information. Statements such as "Yes," "No," or "If necessary" are not informative. Ventilation requirements should be specific as to type and preferred methods. Respirators shall be specified as to type and NIOSH or US Bureau of Mines approval class, ie, "Supplied air," "Organic vapor canister," "Suitable for dusts not more toxic than lead," etc. Protective equipment must be specified as to type and materials of construction.

(i) Section IX. Special Precautions

"Precautionary Statements" shall consist of the label statements selected for use on the container or placard. Additional information on any aspect of safety or health not covered in other sections should be inserted in Section IX. The lower block can contain references to published guides or in-house procedures for handling and storage. Department of Transportation markings and classifications and other freight, handling, or storage requirements and environmental controls can be noted.

(j) Signature and Filing

Finally, the name and address of the responsible person who completed the MSDS and the date of completion are entered. This will facilitate correction of errors and identify a source of additional information.

The MSDS shall be filed in a location readily accessible to workers potentially exposed to the hazardous material. The MSDS can be used as a training aid and basis for discussion during safety meetings and training of new employees. It should assist management by directing attention to the need for specific control engineering, work practices, and protective measures to ensure safe handling and use of the material. It will aid the safety and health staff in planning a safe and healthful work environment and in suggesting appropriate emergency procedures and sources of help in the event of harmful exposure of employees.

MATERIAL SAFETY DATA SHEET

I PRODUCT IDENTIFICATION

MANUFACTURER'S NAME	REGULAR TELEPHONE NO EMERGENCY TELEPHONE NO
ADDRESS	
TRADE NAME	
SYNONYMS	

II HAZARDOUS INGREDIENTS

MATERIAL OR COMPONENT	%	HAZARD DATA

III PHYSICAL DATA

BOILING POINT 760 MM HG		MELTING POINT
SPECIFIC GRAVITY (H_2O=1)		VAPOR PRESSURE
VAPOR DENSITY (AIR=1)		SOLUBILITY IN H_2O % BY WT
% VOLATILES BY VOL		EVAPORATION RATE (BUTYL ACETATE-1)
APPEARANCE AND ODOR		

IV FIRE AND EXPLOSION DATA

FLASH POINT (TEST METHOD)		AUTOIGNITION TEMPERATURE	

FLAMMABLE LIMITS IN AIR, % BY VOL	LOWER		UPPER	

EXTINGUISHING MEDIA	
SPECIAL FIRE FIGHTING PROCEDURES	
UNUSUAL FIRE AND EXPLOSION HAZARD	

V HEALTH HAZARD INFORMATION

HEALTH HAZARD DATA

ROUTES OF EXPOSURE

- INHALATION
- SKIN CONTACT
- SKIN ABSORPTION
- EYE CONTACT
- INGESTION

EFFECTS OF OVEREXPOSURE

- ACUTE OVEREXPOSURE
- CHRONIC OVEREXPOSURE

EMERGENCY AND FIRST AID PROCEDURES

- EYES
- SKIN
- INHALATION
- INGESTION

NOTES TO PHYSICIAN

VI REACTIVITY DATA

CONDITIONS CONTRIBUTING TO INSTABILITY

INCOMPATIBILITY

HAZARDOUS DECOMPOSITION PRODUCTS

CONDITIONS CONTRIBUTING TO HAZARDOUS POLYMERIZATION

VII SPILL OR LEAK PROCEDURES

STEPS TO BE TAKEN IF MATERIAL IS RELEASED OR SPILLED

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RESPIRATORY (SPECIFY IN DETAIL)

EYE

GLOVES

OTHER CLOTHING AND EQUIPMENT

IX SPECIAL PRECAUTIONS

PRECAUTIONARY STATEMENTS	
OTHER HANDLING AND STORAGE REQUIREMENTS	

PREPARED BY ____________________

ADDRESS ____________________

DATE ____________________

XII. TABLES AND FIGURE

TABLE XII-1

PHYSICAL PROPERTIES OF HYDROGEN FLUORIDE

Property	Anhydrous Hydrogen Fluoride		Aqueous Hydrogen Fluoride
	Liquid	Gas	
Color	Colorless	Colorless	Colorless
Odor	Pungent, irritating	Pungent, irritating	Pungent, irritating
Molecular weight (monomer)	20.01	20.01	20.01
	NOTE: Hydrogen fluoride is monomeric only at high temperatures and low partial pressures. At lower temperatures polymers, especially (HF)2 and (HF)6, are formed. However, at room temperature and partial pressures equivalent to the TWA limit, HF is probably monomeric.		
Boiling point, 1 atmosphere	19.5 C	----	Varies with concentration
Melting point	-83.37 C	----	"
Specific gravity 1 atmosphere	1.0 (4 C)	1.27 (34 C, air = 1)	"
Vapor pressure,	42.19 g/sq cm	----	----
70 F (21 C)	4.1kPa	----	----
100 F (38 C)	86.9kPa	----	----
Constant boiling mixture (35.35%)	----	----	120 C
Specific volume 1 atm, 21 C	----	1204.8 ml/g	----
Solubility in water	-------Miscible in all proportions-------		

From references 2,4,5

TABLE XII-2

OCCUPATIONS WITH POTENTIAL EXPOSURE TO HYDROGEN FLUORIDE

- Aircraft workers
- Alkylation plant workers
- Alloy steel cleaners
- Alloy steel makers
- Aluminum fluoride makers
- Aluminum workers
- Ammonium fluoride makers
- Bleachers
- Brass cleaners
- Brewers
- Brick cleaners
- Casting cleaners
- Ceramic workers
- Chemists
- Copper cleaners
- Cryolite makers
- Crystal glass polishers
- Dye makers
- Electric arc welders
- Electroplaters
- Enamel etchers
- Fermentation workers
- Fertilizer makers
- Filter paper makers
- Fluoborate makers
- Fluoride makers
- Fluorine makers
- Fluocarbon makers
- Fluorochemical makers
- Fluosilicate makers
- Freon makers
- Genetron makers
- Glass etchers
- Graphite purifiers
- Hydrogen fluoride workers
- Incandescent lamp frosters
- Isotron makers
- Laundry workers
- Metal cleaners
- Metal polishers
- Neon sign makers
- Oil well acidizers
- Ore dissolvers
- Petroleum refinery workers
- Phosphate rock workers
- Phosphoric acid makers
- Plastic makers
- Polish workers
- Quartz crystal makers
- Rocket fuel handlers
- Rocket fuel makers
- Stainless steel cleaners
- Stainless steel makers
- Steel casting picklers
- Stone cleaners
- Uranium refiners
- Yeast makers

Adapted from reference 202

TABLE XII-3

RELATIONSHIP BETWEEN THE CONCENTRATION OF INHALED HYDROGEN FLUORIDE AND ITS EFFECTS ON ANIMALS

Reference	Exposure Concentration (mg/cu m)	Length of Exposure (hrs)	Animal	Effects
52	540	0.5 -1	Guinea pigs (5)	Death
52	205	0.5 -1	"	"
52	540	1.5 -3	Rabbits (5)	"
52	205	1.5 -3	"	"
52	40	2.0	Guinea pigs (5)	"
52	40	3.0	Rabbits (5)	Physical distress
52	25	24.0	Guinea pigs	Death
52	8	120.0	"	Labored breathing, eye irritation
52	8	186.0 (6 hrs/day)	Rabbits (15)	Death (2), weight loss and anemia (13)
52	8	"	Guinea pigs (21)	Death (7), weight loss and anemia (14)
52	8	"	Doves (4)	Death (1), weight loss and anemia (3)
52	2.5	"	Rabbits (16)	No pathologic changes
52	2.5	"	Guinea pigs (20)	"
52	2.5	"	Doves (3)	"
35	50	0.08-0.25	Rabbits (3)	Mild eye and respiratory irritation
35	50	0.08-0.25	Guinea pigs (3)	"
35	24	0.08-0.25	Rabbits (3)	"
35	24	0.08-0.25	Guinea pigs (3)	"

TABLE XII-3 (CONTINUED)

RELATIONSHIP BETWEEN THE CONCENTRATION OF INHALED HYDROGEN FLUORIDE AND ITS EFFECTS ON ANIMALS

Reference	Exposure Concentration (mg/cu m)	Length of Exposure (hrs)	Animal	Effects
35	24	41.0	Rabbit (1)	Liver and kidney damage
35	3,000	0.08-0.25	Rabbits (3)	Edema or cloudy swelling of organs and tissues
35	3,000	0.08-0.25	Guinea pigs (3)	"
54	15.2	309 (6-8 hrs/day)	Rabbits (8)	Leukocytic infiltration of lung (8), fatty degeneration of liver (2), renal tubular degeneration and necrosis
54	15.2	"	Monkey (1)	Renal tissue degeneration and inflammation
54	15.2	"	Guinea pig (1)	Pulmonary hemorrhages, alveolar exudates, atelectatic areas, liver degeneration
54	15.2	160 (6-8 hrs/day)	"	Death
54	15.2	134 (6-8 hrs/day)	"	"
55	7	180 (6 hrs/day)	Rats (15)	Subcutaneous hemorrhages in feet
55	7	"	Dogs (5)	Hemorrhagic areas in lung (1)
55	25	"	Rats (29)	Death
55	25	"	Mice (18)	"
55	25	"	Dogs (4)	Degenerative testicular changes (4) Moderate hemorrhages and edema of lungs (3)
55	25	"	"	Ulceration of the scrotum
55	25	"	Rabbits (18)	Slight pulmonary hemorrhage (4)

TABLE XII-3 (CONTINUED)

RELATIONSHIP BETWEEN THE CONCENTRATION OF INHALED HYDROGEN FLUORIDE AND ITS EFFECTS ON ANIMALS

Reference	Exposure Concentration (mg/cu m)	Length of Exposure (hrs)	Animal	Effects
58	4,060	0.08	Rats (10)	Respiratory distress, conjunctival and nasal irritation (10), death (5)
58	2,200	0.25	"	"
58	1,670	0.50	"	
58	1,070	1.0	"	"
58	3,540	0.25	Guinea pigs (10)	Death (5)
58	14,900	0.08	Rats (10)	"
58	5,120	0.08	Mice (15)	"

TABLE XII-4

HYDROGEN FLUORIDE EXPOSURE - EFFECT DATA--HUMAN STUDIES

Reference	Exposure Concentration	Number Exposed	Route of Administration	Effects
32	8,000 -80,000 mg/cu m	2	Dermal exposure to 70% HF acid on clothing in chest area, resulting in inhalation exposure	Death from pulmonary edema
29	5 g	1	Dermal exposure to 100% anhydrous HF acid	Second- and third-degree burns, pain, nausea, stupor, mild throat irritation
50	2.4 -6.0 mg/cu m	46	Inhalation of gaseous and particulate fluorides	Slight blurring of bone structure
50	"	4	"	Merging of trabeculae; diffuse structureless appearance of bone
50	"	26	"	Marble-white opacity of bones of the pelvis, lumbar spine, and ribs; irregular vertebral bodies; calcification of pelvis ligaments; irregular periosteal bone formation. Marked restricted movements of the spine
48	3.38 mg/cu m (average) 1.78-7.73 (range)	17	"	Increase or questionable increase in bone density
36	0.7 mg/cu m	-	Inhalation of HF by etchers and welders	Nosebleeds

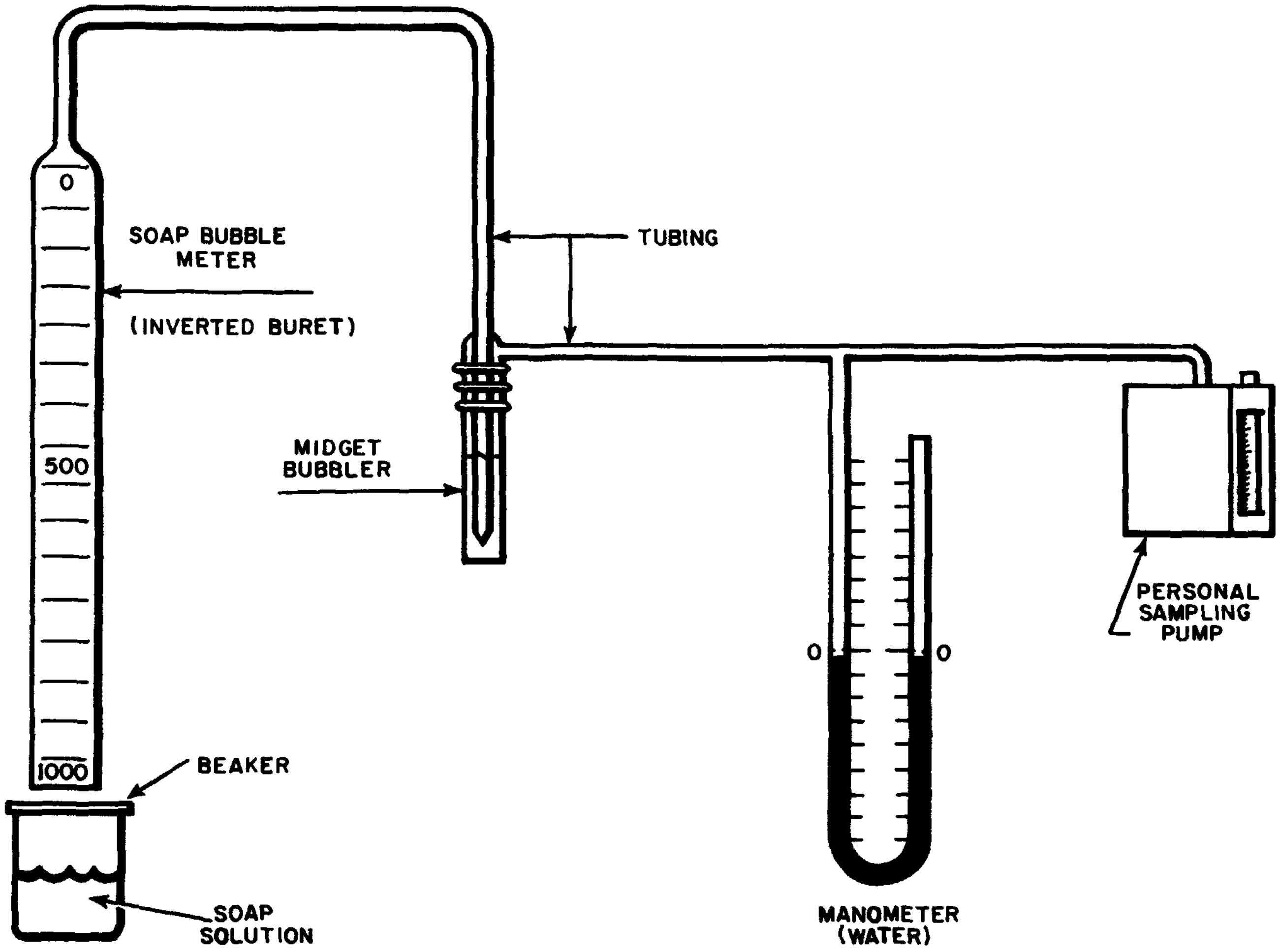
TABLE XII-4 (CONTINUED)

HYDROGEN FLUORIDE EXPOSURE - EFFECT DATA--HUMAN STUDIES

Reference	Exposure Concentration	Number Exposed	Route of Administration	Effects
35	100 mg/cu m	2	Inhalation of HF for less than 1 minute	Smarting of exposed skin, marked conjunctival and respiratory irritation
35	50 mg/cu m	2	Inhalation of HF for unspecified time	Marked conjunctival and respiratory irritation
35	26 mg/cu m	2	Inhalation of HF for several minutes	Mild eye and nose irritation
26	2.12 mg/cu m (average)	1	Inhalation of HF 6 hrs/day, 5 days/ week for 15 days	Very slight irritation of eyes and nose, slight cutaneous erythema
26	2.78 mg/cu m (average)	1	Inhalation of HF 6 hrs/day, 5 days/ week for 10 days	"
26	2.23 mg/cu m (average)	1	Inhalation of HF 6 hrs/day, 5 days/ week for 30 days	"
26	3.46 mg/cu m (average)	1	Inhalation of HF 6 hrs/day, 5 days/ week for 50 days	"
26	3.89 mg/cu m (average)	1	Inhalation of HF 6 hrs/day, 5 days/ week for 25 days	"

Figure XII-1

CALIBRATION SETUP FOR PERSONAL SAMPLING PUMP WITH MIDGET BUBBLER



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