

# Occupational Health Guideline for Hydrogen Fluoride

## INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

## SUBSTANCE IDENTIFICATION

- Formula: HF
- Synonyms: Anhydrous hydrofluoric acid; HF-A
- Appearance and odor: Colorless, fuming liquid or gas with a strong irritating odor.

## PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for hydrogen fluoride is 3 parts of hydrogen fluoride per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 2 milligrams of hydrogen fluoride per cubic meter of air ( $\text{mg}/\text{m}^3$ ). NIOSH has recommended that the permissible exposure limit be changed to 2.5  $\text{mg}/\text{m}^3$  averaged over a work shift of not more than 10 hours per day, 40 hours per week, with a ceiling level of 5  $\text{mg}/\text{m}^3$  averaged over a 15-minute period. The NIOSH Criteria Document for Hydrogen Fluoride should be consulted for more detailed information.

## HEALTH HAZARD INFORMATION

### • Routes of exposure

Hydrogen fluoride can affect the body if it is inhaled, comes in contact with the eyes or skin, or is swallowed. It may enter the body through the skin.

### • Effects of overexposure

**1. Short-term Exposure:** Hydrogen fluoride liquid or vapor causes severe irritation and deep-seated burns of the eye and eye lids if it comes in contact with the eyes. If the chemical is not removed immediately, permanent

visual defects or blindness may result. When lower concentrations (20% or less) come into contact with the skin, the resulting burns do not usually become apparent for several hours. Skin contact with higher concentrations is usually apparent in a much shorter period, if not immediately. The skin burns may be very severe and painful. Hydrofluoric acid is a severe irritant to the nose, throat, and lungs. Severe exposure causes rapid inflammation and congestion of the lungs. Breathing difficulties may not occur until some hours after exposure has ceased. Death may occur from breathing this chemical. If swallowed, hydrofluoric acid will immediately cause severe damage to the throat and stomach.

**2. Long-term Exposure:** Prolonged or repeated exposure to lower concentrations of hydrogen fluoride vapor may cause changes in the bones. Exposure to low concentrations of vapors of hydrogen fluoride may also cause chronic irritation and congestion of the nose, throat, and bronchial tubes.

**3. Reporting Signs and Symptoms:** A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to hydrogen fluoride.

### • Recommended medical surveillance

The following medical procedures should be made available to each employee who is exposed to hydrogen fluoride at potentially hazardous levels:

#### 1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the eyes, respiratory tract, central nervous system, skeletal system, and the kidneys should be stressed. The skin should be examined for evidence of chronic disorders.

—Urinalysis: Since kidney damage has been observed in acute overexposures to hydrogen fluoride, a urinalysis should be obtained to include, at a minimum, specific gravity, albumin, glucose, and a microscopic on centri-

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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fuged sediment. An analysis for fluoride should be performed.

—Pelvic roentgenogram: Hydrogen fluoride may cause skeletal abnormalities. A radiologic examination of the male pelvis with proper gonadal shielding should be conducted at the time of the preplacement examination and when indicated by analysis of the results of the urinary hydrogen fluoride tests.

—Eye disease: Hydrogen fluoride is a severe eye irritant and may cause tissue damage. Those with pre-existing eye problems may be at increased risk from exposure.

—14" x 17" chest roentgenogram: Hydrogen fluoride may cause human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Hydrogen fluoride is a respiratory irritant. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

—Skin disease: Hydrogen fluoride can cause dermatitis on prolonged exposure to concentrations from 1.8 to 8.1 mg/m<sup>3</sup>. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

**2. Periodic Medical Examination:** The aforementioned medical examinations should be repeated on an annual basis, except that the radiologic examination of the pelvis should be conducted only when clinically indicated.

#### • Summary of toxicology

Hydrogen fluoride as a gas is a severe respiratory irritant, and in solution causes severe and painful burns of the skin. Animals repeatedly exposed to 17 ppm showed damage to the lungs, liver, and kidneys, but at 8.6 ppm there was only occasional lung injury. Fatalities occurred in 3 of 6 workers exposed to spills of 70% solutions on the skin and inhalation of the vapor; despite prompt showering with water for skin burns, death from pulmonary edema occurred 2 hours after exposure. A chemist, splashed on the face and upper extremities with hydrogen fluoride, developed pulmonary edema 3 hours after exposure and died 10 hours later. In human subjects, 120 ppm was the highest concentration that could be tolerated for 1 minute, because of the onset of conjunctival and respiratory irritation with stinging of the skin. Repeated experimental human exposures to concentrations of 2 ppm for 6 hours daily caused a slight stinging of the eyes and skin of the face, with nasal irritation. Repeated exposures to low concentrations at work may produce chronic irritation of the nose, throat, and bronchi. Hydrogen fluoride solutions in contact with skin, if untreated, result in marked tissue destruction; the fluoride ion readily penetrates skin and deep tissue, causing necrosis of soft tissues and decalcification of bone. When skin contact is with solutions of less than 50% hydrogen fluoride, the burns do not become manifest immediately; burns from solutions stronger than 50% and anhydrous HF are felt in a matter of minutes, and because fluoride ions penetrate the skin readily, necrosis of deep tissue and damage to

the bone may occur. Severe eye injuries from splashes may occur. In one case of eye burns from a fine spray of hydrofluoric acid in the face, considerable loss of corneal epithelium occurred despite immediate and copious flushing with water and irrigation for 3 hours with a 0.5% solution of benzethonium chloride; within 19 days there was recovery of normal vision.

## CHEMICAL AND PHYSICAL PROPERTIES

### • Physical data

1. Molecular weight: 20
2. Boiling point (760 mm Hg): 19.5 C (67.1 F)
3. Specific gravity (water = 1): 1.0
4. Vapor density (air = 1 at boiling point of hydrogen fluoride): 0.7
5. Melting point: -83.4 C (-118 F)
6. Vapor pressure at 20 C (68 F): 760 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): Miscible in all proportions

8. Evaporation rate (butyl acetate = 1): Data not available

### • Reactivity

1. Conditions contributing to instability: Heat
2. Incompatibilities: Contact of hydrogen fluoride (liquid or gas) with metals, concrete, glass, and ceramics causes severe corrosion. Contact with metals may form flammable hydrogen gas.

3. Hazardous decomposition products: None

4. Special precautions: Liquid or gaseous hydrogen fluoride will attack some forms of plastics, rubber, and coatings. It will also attack glass and other ceramic materials.

### • Flammability

1. Not combustible

### • Warning properties

1. Odor Threshold: The Manufacturing Chemists Association reports that the vapor has a sharp and penetrating odor, but no quantitative information is available concerning the odor threshold.

2. Eye Irritation Level: Grant states that "air containing as little as 5 ppm (hydrogen fluoride) causes irritation of the eyes."

3. Other Information: According to Grant, irritation of the nose occurs at a concentration as low as 5 ppm.

4. Evaluation of Warning Properties: Since hydrogen fluoride can be detected through its irritant effects at a concentration slightly above the permissible exposure limit, it is treated as a material with adequate warning properties.

## MONITORING AND MEASUREMENT PROCEDURES

### • Eight-Hour Exposure Evaluation

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30

minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

#### • Ceiling Evaluation

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of hydrogen fluoride. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

#### • Method

Sampling and analyses may be performed by collection of hydrogen fluoride in a bubbler, followed by dilution with a buffer, and analysis with an ion-specific electrode. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure hydrogen fluoride may be used. An analytical method for hydrogen fluoride is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

## RESPIRATORS

• Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

• In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

## PERSONAL PROTECTIVE EQUIPMENT

• Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with

liquid hydrogen fluoride or solutions containing hydrogen fluoride.

• Clothing contaminated with hydrogen fluoride should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of hydrogen fluoride from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the hydrogen fluoride, the person performing the operation should be informed of hydrogen fluoride's hazardous properties.

• Where there is any possibility of exposure of an employee's body to liquid hydrogen fluoride or solutions containing hydrogen fluoride, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

• Non-impervious clothing which becomes contaminated with hydrogen fluoride should be removed immediately and not reworn until the hydrogen fluoride is removed from the clothing.

• Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid hydrogen fluoride or solutions containing hydrogen fluoride contacting the eyes.

• Where there is any possibility that employees' eyes may be exposed to liquid hydrogen fluoride or solutions containing hydrogen fluoride, an eye-wash fountain should be provided within the immediate work area for emergency use.

• Whenever hydrogen fluoride is accidentally released into the workplace air, employees should be required to immediately evacuate the area.

## SANITATION

• Skin that becomes contaminated with hydrogen fluoride should be immediately washed or showered to remove any hydrogen fluoride.

• Eating and smoking should not be permitted in areas where liquid hydrogen fluoride or solutions containing hydrogen fluoride are handled, processed, or stored.

• Employees who handle liquid hydrogen fluoride or solutions containing hydrogen fluoride should wash their hands thoroughly before eating, smoking, or using toilet facilities.

## COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to hydrogen fluoride may occur and control methods which may be effective in each case:

<b>Operation</b>	<b>Controls</b>	<b>Operation</b>	<b>Controls</b>
Use in manufacture of chlorofluorohydrocarbons for application as refrigerant fluids, aerosol propellants, specialty solvents, high-performance plastics, and foaming agents	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment	Use of anhydrous acid in separation and purification of uranium isotopes	Process enclosure; local exhaust ventilation; personal protective equipment
Use of aqueous acid in cleaning sandstone and marble; use as a pickling agent for stainless steel and other metals; use as a cleaner in meat packing industry	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment	Use in manufacture of insecticides; use of aqueous acid in treating textiles to remove trace metals	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use of anhydrous acid in manufacture of aluminum fluoride and synthetic cryolite for reduction of aluminum oxide to aluminum	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment	Use of anhydrous acid in production of fluorosilicone products	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use of aqueous acid in electroplating operations	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment	Use of aqueous acid in preparation of microelectronic circuits and quartz crystals for radio oscillators	Process enclosure; local exhaust ventilation; personal protective equipment
Liberation from fertilizer manufacture	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment	Use of aqueous acid in manufacture of laundry sours and stain removers	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use of anhydrous acid as a catalyst in alkylation of petroleum fractions to produce high-octane fuels	Process enclosure; local exhaust ventilation; personal protective equipment	Use of aqueous acid in extraction and purification of minerals	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use of aqueous acid in etching, frosting, and polishing glassware and ceramics	Process enclosure; local exhaust ventilation; personal protective equipment	Use of anhydrous acid in manufacture of pharmaceuticals and special dyes	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment
Use as an acidizing agent during injection of acid into oil wells	Process enclosure; local exhaust ventilation; personal protective equipment		
Use of aqueous acid in removal of sand and scale from foundry castings	General dilution ventilation; process enclosure; local exhaust ventilation; personal protective equipment		

## **EMERGENCY FIRST AID PROCEDURES**

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

- **Eye Exposure**

If liquid hydrogen fluoride or solutions containing hydrogen fluoride get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

- **Skin Exposure**

If liquid hydrogen fluoride or solutions containing hydrogen fluoride get on the skin, immediately flush the contaminated skin with water for a considerable time. If liquid hydrogen fluoride or solutions containing hydrogen fluoride penetrate through the clothing, remove the clothing immediately and flush the skin with water for a considerable time. Get medical attention immediately.

### • Breathing

If a person breathes in large amounts of hydrogen fluoride, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

### • Swallowing

If liquid hydrogen fluoride or solutions containing hydrogen fluoride have been swallowed and the person is conscious, give him large quantities of water immediately to dilute the hydrogen fluoride. Do not attempt to make the exposed person vomit. Get medical attention immediately.

### • Rescue

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

## SPILL AND LEAK PROCEDURES

- Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

- If hydrogen fluoride is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak to disperse gas.
2. If in the gaseous form, stop flow of gas. If source of leak is a cylinder and the leak cannot be stopped in place, remove the leaking cylinder to a safe place in the open air, and repair the leak or allow the cylinder to empty.
3. If in the liquid form, allow to vaporize and disperse the gas.

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## RESPIRATORY PROTECTION FOR HYDROGEN FLUORIDE

Condition	Minimum Respiratory Protection* Required Above 3 ppm
Gas or Vapor Concentration	
20 ppm or less	<p>A chemical cartridge respirator with a full facepiece and cartridge(s) providing protection against hydrogen fluoride.</p> <p>A gas mask with a chin-style or a front- or back-mounted canister and filter providing protection against hydrogen fluoride.</p> <p>Any supplied-air respirator with a full facepiece, helmet, or hood.</p> <p>Any self-contained breathing apparatus with a full facepiece.</p>
Greater than 20 ppm** or entry and escape from unknown concentrations	<p>Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.</p> <p>A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.</p>
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	<p>Any gas mask providing protection against hydrogen fluoride.</p> <p>Any escape self-contained breathing apparatus.</p>

\*Only NIOSH-approved or MSHA-approved equipment should be used.

\*\*Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of hydrogen fluoride; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 20 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.