UCSC Laboratory Safety Services
Providing a little slug of information on . . .

Hydrofluoric Acid
Chemical Safety Information Sheet

Chemical Information Overview

Hydrofluoric acid (HF) differs from other acids because the fluoride ion readily penetrates the skin, causing destruction of deep tissue layers, including bone. Pain associated with exposure to solutions of HF (1-50%) may be delayed for 1-24 hours. If HF is not rapidly neutralized and the fluoride ion bound, tissue destruction may continue for days and result in limb loss or death. HF is similar to other acids in that the initial extent of a burn depends on the concentration, the temperature, and the duration of contact with the acid.

Chemical Name: Hydrofluoric Acid
Chemical Family: Inorganic Acid
Chemical Formula: HF
Molecular Weight: 20.0
CAS Number: 7664-39-3

Synonyms: HF, Hydrofluoride, Fluoric Acid

Physical Data

Description: Colorless gas or fuming liquid (below 153°F) with a strong, irritating odor.
Boiling Point: 153° F (67° C)
Specific Gravity: 1.2 (H_2O = 1)
Ionization Potential: 15.98 eV

Solubility in Water: Miscible
Vapor Density: 2.21 (Air = 1)
Odor Threshold: 0.5 – 3 ppm (caution: reported range is very broad)

Exposure Limits

ACGIH Threshold Limit Value (TLV): Listed as Hydrogen fluoride, as F: (ACGIH, 2000)
- 8-Hour Time Weighted Average (TWA): Not Listed
- Ceiling: 3 ppm (2.3 mg/m^3)
- Skin Notation: Not Listed
- Carcinogen: Not Listed
- TLV Ceiling value based on irritation with possible burns and effects to bone, teeth, and fluorosis.

OSHA Permissible Exposure Limit (PEL): Listed as Hydrogen fluoride (as F) (OSHA, 1996a)
- 8-Hour Time Weighted Average (TWA): 3 ppm
- Ceiling: Not Listed

NIOSH Recommended Exposure Limit (REL): (NIOSH, 1996)
- 8-Hour Time Weighted Average (TWA): 3 ppm (2.3 mg/m^3)
- Ceiling: 6 ppm (5 mg/m^3) (15-minute)
- Skin Notation: Not Listed
- Carcinogen: Not Listed
- IDLH VALUE: (Immediately Dangerous To Life and Health): 30 ppm

NOTE: A TWA concentration is for an 8-hour workday (ACGIH-TLV, OSHA-PEL) and up to a 10-hour workday (NIOSH-REL) during a 40-hour workweek. A STEL value is a 15-minute TWA exposure that should not be exceeded at any time during a workday. A Ceiling value should never be exceeded for even an “instantaneous” exposure period.

Health Hazard Data: Dermal Exposure

DERMAL EXPOSURE - HF is an inorganic acid that is highly corrosive and readily penetrates the skin, causing deep tissue layer destruction. Severity and rapidity of onset of signs and symptoms depends on the concentration, duration of exposure, and penetrability of the exposed tissue. Pain may be delayed.

1. CONCENTRATIONS LESS THAN 20% - Erythema and pain may be delayed up to 24 hours, often not reported until tissue damage is extreme. In one study, 7% HF produced symptoms in 1 to several hours, 12% HF in less than one hour, and 14.5% HF immediately.

2. CONCENTRATIONS 20 TO 50% - Erythema and pain may be delayed from 1 to 8 hours, and is often not reported until tissue damage is extreme.

3. CONCENTRATIONS GREATER THAN 50% - Produces immediate burning, erythema, and tissue damage.

DECONTAMINATION – Remove all exposed clothing taking necessary precautions to prevent self-exposure. Immediately wash all exposed areas with copious amounts of water.

CALCIUM GLUCONATE OR CARBONATE GEL – Application of 2.5 to 33% calcium gluconate or carbonate gel or slurry, either placed into a surgical glove into which the affected extremity is then placed, or rubbed into the burn, is recommended. This therapy is more easily administered and less painful than infiltration. *Use calcium gluconate for dermal treatment only.*

CALCIUM GLUCONATE INFILTRATION – **(Medical Assistance)** – Continued tissue destruction and pain may be minimized by subcutaneous administration of calcium gluconate. Consider infiltration with CALCIUM GLUCONATE if (1) exposure results in immediate tissue damage or (2) erythema and pain persist following adequate irrigation. Infiltrate each square centimeter of affected dermis and subcutaneous tissue with about 0.5 mL of 10% CALCIUM GLUCONATE using a 30 gauge needle. Repeat as needed to control pain. Split or remove nails to treat nail bed burns. The earlier this is administered, the more rapidly symptoms resolve. CAUTION: Avoid administering large volumes of subcutaneous calcium gluconate as this will result in decreased tissue perfusion and potential necrosis.

DO NOT USE CALCIUM CHLORIDE – Calcium chloride is irritating to the tissues and may cause injury.

Health Hazard Data: Other Routes of Exposure

SYSTEMIC TOXICITY – Systemic fluoride toxicity may result from ingestion, inhalation, or extensive dermal burns. Hypocalcemia, hypomagnesemia, hyperkalemia (potassium), pulmonary edema, metabolic acidosis, ventricular arrhythmias, and death are possible.

EYE EXPOSURE – May result in severe ocular damage with concentrations greater than 0.5%. Fume exposure commonly causes eye irritation and can also cause ocular injury. Signs and symptoms may be delayed.

ORAL EXPOSURE – Ingestion may result in vomiting and abdominal pain; painful necrotic lesions, hemorrhagic gastritis, and pancreatitis have been reported after significant exposure. Rectal administration has caused acute colitis with perforation.

INHALATION EXPOSURE – Inhalation of hydrofluoric acid vapors may cause severe throat irritation, cough, dyspnea, cyanosis, lung injury and pulmonary edema resulting in death.

Toxicity Data: LD50, LC50

Lowest Lethal Dose, Human LCLo: 50 ppm/30 min.

Inhalation, Rat LC50: 1278 ppm/1hr.
Inhalation, Mouse LC50: 500 ppm/1hr.
Inhalation, Guinea Pig LC50: 4327 ppm/15 min.
Inhalation, Monkey 1780 ppm/1 hr.

Descriptive Term	*LD50 wt/kg oral dose in rats*	*LC50 4-hr inhalation dose in rats*
Extremely Toxic	≤ 1 mg	< 10 ppm
Highly Toxic	1-50 mg	10-100 ppm
Moderately Toxic	50-500 mg	100-1,000 ppm
Slightly Toxic	0.5-5 g	1,000-10,000 ppm
Practically Nontoxic	5-15 g	10,000-100,000 ppm
Relatively Harmless	≥ 15 g	> 100,000 ppm

Toxilogical Mechanism

Several proposed toxicological mechanisms.
1. Fluoride binds to metal-containing enzymes, thereby inactivating them.
2. Fluoride binds to calcium, resulting in severe hypocalcemia.
3. Fluoride binds to potassium and magnesium ions leading to myocardial irritability and arrhythmia.
4. Fluoride may be directly toxic to the CNS.

Minimum Lethal Exposure

ORAL

- Death has occurred after ingestion of 1.5 grams of hydrofluoric acid (concentration unknown) within 6.5 hours of ingestion. Postmortem findings in this case revealed no gross tissue damage and a liver fluoride level of 165 micrograms/100 gram.
- A 33-year-old man who ingested 3 to 4 ounces of a rust remover (unstated HF concentration) died within 45 to 60 minutes. At autopsy, severe mucosal edema of the stomach and hemorrhage and necrosis of the pancreas were noted. The postmortem blood fluoride level was 56.2 milligrams/liter.
- Ingestion of 15 milliliters of a 9 percent solution was reported to cause death.

DERMAL

- A dermal exposure to 70 percent hydrofluoric acid over a 2.5 percent total body surface area resulted in death. The serum calcium level was 2.2 milligrams/deciliter.
- An adult patient who developed 25 percent total body surface area second degree burns after exposure to a 70 percent hydrofluoric acid preparation died in cardiac arrest. Ionized serum calcium level was 1.7 milligrams per deciliter (normal: 4 to 4.8) immediately premortem.
- Two workers died following a splash exposure of 70 percent hydrofluoric acid to the face, chest, arms and legs. Both workers were promptly removed from site of exposure. Clothing was removed and burns were initially treated at the workplace with a cold shower and alcohol was applied to burn areas. Suitable protective clothing was not worn at the workplace.
- A woman died from severe chemical burns of the skin and lungs, with intense pulmonary hemorrhagic edema after having acid thrown onto her face during an attack.
- A patient with HF burns involving 8 percent of his body died from intractable cardiac arrhythmia secondary to the depletion of ionized calcium.

INHALATION

- Estimates of the lowest lethal concentrations for hydrogen fluoride range from 50-250 ppm for 5-minute exposure and are based on accidental, voluntary and occupational exposure information.

Handling and PERSONAL PROTECTIVE EQUIPMENT

1) Familiarize yourself with the hazards specific to HF before handling.
2) Always handle HF in:
   - ✓ *A properly functioning fume hood*
   - ✓ *An area equipped with a Safety Shower/Eye Wash*
3) Recommended Personal Protective Equipment:
   - ✓ Goggles
   - ✓ Face shield (plastic)
   - ✓ Gloves: Thin disposable gloves (such as 4, 6, or 8 mil blue Nitrile glove) used in laboratory operations provide a contact barrier only and should be disposed of immediately when contamination is suspected. Thicker (10-20 mil) PVC or neoprene gloves provide good resistance to HF but do not provide the necessary dexterity for most lab procedures. Thinner PVC or poly ("food" handling) gloves can provide some resistance to HF, but should also be changed immediately at the first sign of contamination. Disposable gloves should never be worn without double gloving because of the potential for pinholes and exposure. A combination of double gloves, Nitrile and poly, can be used to provide greater protection from a broader range of materials.
   - ✓ Acid resistant apron
   - ✓ Long pants, sleeves, and closed toe shoes (always required when working with corrosives)
4) Calcium Gluconate should be available for skin treatment.

Incompatibles and Storage

Store in a cool, dry place away from incompatible materials. HF reacts with many materials therefore avoid contact with glass, concrete, metals, water, other acids, oxidizers, reducers, alkalis, combustibles, organics and ceramics. Store in containers made of polyethylene or fluorocarbon plastic, lead, or platinum. Place storage bottles in polyethylene secondary containment trays.

Never store HF in glass containers.

Spills

Ensure all areas where HF is used are equipped with proper spill response equipment. Small spills can be neutralized by covering with magnesium sulfate (dry) and absorbed with spill control pads or other absorbent materials. Add sodium bicarbonate or magnesium oxide to any absorbent and place in a plastic container for disposal. Wash the spill site with a sodium bicarbonate solution.

Absorbents that can be used which are not reactive to HF include vermiculite and 3M Universal Sorbent. If the spill is large, in a confined space, or in an area where there is not adequate ventilation, evacuate the room and immediately report the spill to 911.

Fire and Explosion Hazard

Hydrogen fluoride is non-combustible, but may create irritating and corrosive fumes of fluorides when heated or in combination with steam or water. Since hydrogen fluoride does not burn, use an extinguishing agent suitable for surrounding fire. Use water to absorb fumes and keep containers cool. Heat released when water or steam combines with hydrogen fluoride or hydrofluoric acid could be hazardous. For fires involving hydrofluoric acid, apply water in flooding quantities. Hydrofluoric acid and various metals may form hydrogen (extremely flammable gas) creating a fire hazard.

Flammability Class: Nonflammable Gas
Flash Point: NA
Lower Explosion Limit: NA
Upper Explosion Limit: NA

HYDROFLUORIC ACID FATALITY TO LAB WORKER IN PERTH

Extract from Australian Institute of Occupational Hygienists Newsletter, December 1994:

An accident in Perth highlighted just how hazardous this acid can be and it is worth recounting for the benefit of any lab working or hygienists whose work may involve advising others who use this substance.

On November 12, a 37 year old man died in the Intensive Care Unit of Fremantle Hospital after he accidentally splashed about 100 ml of a 70% solution on his right leg on October 28. It was estimated that the extent of the spill covered about 10% of his total body area. The individual was working as a technician in a small paleontology laboratory, which was attached to a private residence. HF is used in the industry to digest silicates in ore samples. The victim immediately attempted to remove the spill from his clothing hosing himself down with a hose attached to a sink in the laboratory. He then ran from the laboratory to the swimming pool in the garden, and he remained in the pool until the ambulance arrived within the hour. At the time he appeared confused, possibly as a result of shock.

The following week his right leg was amputated, however despite this, the individual eventually succumbed to the toxic effects of the hydrofluoric acid 2 weeks after the initial spill. There are a number of points that need to be emphasized as a result of this, which are relevant to all users of HF:

BY WHAT MECHANISM DOES HYDROFLUORIC ACID CAUSE DEATH?

Posted By: William M. Rich, MD Faculty, University Med. Center

Hydrogen fluoride is a gas which when in solution with water forms hydrofluoric acid, HF. Although a weak acid, i.e., it is not strongly disassociated, is used to etch glass. Like it's sister, HCl acid, it reacts with water with the release of heat and can cause burns on the skin. Hydrofluoric acid has an even more detrimental effect that can affect many internal structures. Fatalities have been reported from a skin exposure to as little as 2.5% of body surface area. The weak disassociation allows it to be absorbed through the skin as the intact molecule.

Once it penetrates the skin it slowly disassociates into the hydrogen ion and fluoride ion. The fluoride ion affects tissue integrity and metabolism by liquefaction necrosis, decalcification and destruction of bone, and production of insoluble salts. Loss of calcium, (hypocalcemia), results from precipitation of calcium form the blood as CaF2. This will eventually result in loss of calcium from the bones to try to equilibrate the decreased serum calcium. This may be a delayed fatal event. The rapid development of hypocalcemia can be rapidly fatal because calcium is important for muscles, including cardiac muscle, to function properly. Without calcium, many metabolic pathways breakdown.

Fluoride from any source has the same toxicity. A mass poisoning occurred at a state hospital many years ago when a bug poison containing NaF was mistaken for powdered milk and added to scrambled eggs. There were reported to be 47 deaths. In some regions of the country the levels of fluoride in the water are too high and this causes mottling of the teeth and loss of calcium from the bones.

Inhalation of HF produces an immediate injury to the lining of the lungs with hemorrhage pulmonary edema and death. It may take only about 5 minutes of exposure to inhaled HF to produce death in a couple of hours.

All in all, fluoride from whatever source can be very dangerous.