The hydrofluoric acid hazard

Hydrofluoric acid (HF) is considered more toxic than cyanide gas. The IDLH (Immediately dangerous to life or health) concentration value given by NIOSH for HF gas is 25 mg/m^3. Note 25 mg is about the mass of a housefly and a cubic meter is the volume of a cube that is a bit more than three feet on an edge.

The origin of the toxicity of HF is two-fold: It readily penetrates the skin, and it has a high affinity for calcium ion. Thus HF burns go deep, and the HF steals Ca^{2+} from tissues (causing them to die and become necrotic) and from bone (causing bone density loss). To make matters worse, HF burns can take a few hours to develop, so the severity of the burn may not be immediately apparent after a spill.

HF should always be handled in a certified chemical fume hood, and the operator should be wearing proper Personal Protective Equipment (PPE). If spilled on the body, it should be rinsed off immediately with copious quantities of water, followed by application of an HF antidote gel (see the section below on First Aid measures).

Protecting yourself when working with HF

Personal protective equipment (PPE) should always be worn when working with HF:

Eye protection: Laboratory-grade safety glasses or goggles should be worn, under a face shield.

Gloves: You should double-glove when working with HF: long (elbow-length) butyl rubber gloves should be worn over nitrile gloves.

Lab coat/apron: Wear a chemical lab coat under a chemical apron. No open toed sandals, shorts or skirts when doing chemistry. Wear long pants that cover the top opening of the shoes.

Cleaning up HF spills

For HF spills, buckets of calcium carbonate powder are located under each etching hood. Calcium carbonate neutralizes HF via the following reaction:

$$2HF_{(aq)} + CaCO_{3(s)} \rightarrow CO_{2(g)} + H_2O_{(l)} + CaF_{2(s)}$$

If you spill HF on the floor or the bench, CLEAN IT UP IMMEDIATELY.
To clean an HF spill, pour calcium carbonate powder or sodium bicarbonate (baking soda) on the spill. Let it react. Continue adding the neutralizing agent until the reaction (bubbling) stops.
After an hour, when the powder has absorbed the entire HF spill, wipe it up and dispose of all the paper towels used as HAZARDOUS WASTE. Put the trash into

a ziploc bag and fill out and attach a waste tag. This bag can go into the waste storage hood.

Guidelines for using HF in an electrochemical or chemical etching experiment

IT IS A STANDARD PRACTICE IN OUR LAB TO NEVER WORK WITH HF (ETCH OR PREPARE SOLUTIONS) ALONE (WITHOUT SOMEONE ELSE IN THE LAB NEARBY).

Before you do your first etch, view the video "etching 101" at:

https://www.youtube.com/watch?v=KpCpDq_K8Ts

Lab coats, apron, face shield, and gloves should be worn at all times when etching or handling etch cells that contain HF (see above).

Always keep HF bottles (and HF waste containers) capped even if you intend to use them again in a few minutes. Secure the cap before you pick up and move a bottle containing HF.

In addition to distinctive labeling indicating the contents (HF, ethanol, etc), we color-code all bottles, pipettes, and syringes that contain HF with a strip of red tape. Waste containers also have white tape to indicate they contain waste. We also size-code containers: HF waste bottles are 1L containers and HF reagent bottles are 500 or 250 mL.

A container of HF should always be placed within a secondary container. Paper matting does not count as secondary containment.

Material Safety Data Sheet (MSDS) for hydrofluoric acid

taken from the Mallincrodt Baker, Inc. MSDS

Hazards Identification
Emergency Overview

POISON! DANGER! CORROSIVE. EXTREMELY HAZARDOUS LIQUID AND VAPOR. CAUSES SEVERE BURNS WHICH MAY NOT BE IMMEDIATELY PAINFUL OR VISIBLE. MAY BE FATAL IF SWALLOWED OR INHALED. LIQUID AND VAPOR CAN BURN SKIN, EYES AND RESPIRATORY TRACT. CAUSES BONE DAMAGE. REACTION WITH CERTAIN METALS GENERATES FLAMMABLE AND POTENTIALLY EXPLOSIVE HYDROGEN GAS.

J.T. Baker SAF-T-DATA(tm) Ratings

Health Rating: 4 - Extreme (Poison)
Flammability Rating: 0 - None
Reactivity Rating: 2 - Moderate
Contact Rating: 4 - Extreme (Corrosive)
Lab Protective Equip: GOGGLES & SHIELD; LAB COAT & APRON; VENT HOOD; PROPER GLOVES
Storage Color Code: White (Corrosive)

Potential health effects of HF

Exposure to hydrofluoric acid can produce harmful health effects that may not be immediately apparent.

Inhalation of HF:
Severely corrosive to the respiratory tract. May cause sore throat, coughing, labored breathing and lung congestion/inflammation.

Ingestion of HF:
Corrosive. May cause sore throat, abdominal pain, diarrhea, vomiting, severe burns of the digestive tract, and kidney dysfunction.

Skin Contact with HF:
Corrosive to the skin. Skin contact causes serious skin burns which may not be immediately apparent or painful. Symptoms may be delayed 8 hours or longer. The fluoride ion readily penetrates the skin causing destruction of deep tissue layers and even bone.

Eye Contact with HF:
Corrosive to the eyes. Symptoms of redness, pain, blurred vision, and permanent eye damage may occur.

Chronic Exposure to HF:

Intake of more than 6 mg of fluorine per day may result in fluorosis, bone and joint damage. Hypocalcemia and hypomagnesemia can occur from absorption of fluoride ion into blood stream.

Aggravation of Pre-existing Conditions:
Persons with pre-existing skin disorders, eye problems, or impaired kidney or respiratory function may be more susceptible to the effects of exposure to HF.

First Aid measures for HF contact

Inhalation of HF:
Get medical help immediately. If patient is unconscious, give artificial respiration or use inhalator. Keep patient warm and resting, and send to hospital after first aid is complete.

Ingestion of HF:
If swallowed, DO NOT INDUCE VOMITING. Give large quantities of water. Never give anything by mouth to an unconscious person. Get medical attention immediately.

Skin Contact with HF:
Remove the victim from the contaminated area and immediately place him under a safety shower or wash him with a water hose, whichever is available.
Remove all contaminated clothing. Handle all HF-contaminated material with gloves made of appropriate material, such as PVC or neoprene
Keep washing with large amounts of water for a minimum of 15 minutes.
Have someone make arrangements for medical attention while you continue flushing the affected area with water.
If HF antidote gel (2.5% calcium gluconate in a water-soluble gel) is available, limit the washing to five minutes and massage the gel into the affected area.
Seek medical attention as soon as possible for all burns regardless of how minor they may appear initially.

HF ANTIDOTE GEL:
This is calcium gluconate dissolved in a water-soluble gel
Distributed by Pharmascience Inc.
8400 Darnley Rd. Montreal, Canada. H4T 1M4
Phone: (514) 340 - 1114
Fax: (514) 342 - 7764
U.S. (Buffalo, NY) distributor: 1-800-207-4477

ALTERNATIVES TO CALCIUM GLUCONATE GEL
Immerse the burned area in a solution of 0.2% iced aqueous Hyamine 1622 or 0.13% iced aqueous Zephiran Chloride. If immersion is not practical, towels should be soaked with one of the above solutions and used as compresses for the burn area. Ideally compresses should be changed every 2 minutes. Hyamine 1622 is a trade name for tetracaine benzethonium chloride, Merck Index

Monograph 1078, a quaternary ammonium compound sold by Rohm & Haas, Philadelphia. Zephiran Chloride is a trade name for benzalkonium chloride, Merck Index Monograph 1059, also a quaternary ammonium compound, sold by Sanofi-Synthelabo Inc., New York, NY.

Eye Contact with HF:
Irrigate eyes for at least 30 minutes with copious quantities of water, keeping the eyelids apart and away from eyeballs during irrigation.
Get competent medical attention immediately, preferably an eye specialist.
If a physician is not immediately available, apply one or two drops of ophthalmic anesthetic, (e.g., 0.5% Pontocaine Hydrochloride solution).
Do not use oily drops, ointment or HF skin burn treatments. Place ice pack on eyes until reaching emergency room.

Note to Physician on treatment of HF burns:

General: For burns of moderate areas, (greater than 8 square inches), ingestion and significant inhalation exposure, severe systemic effects may occur, and admission to a critical care unit should be considered. Monitor and correct for hypocalcemia, cardiac arrhythmias, hypomagnesemia and hyperkalemia. In some cases renal dialysis may be indicated.

Inhalation: Treat as chemical pneumonia. Monitor for hypocalcemia, 2.5% calcium gluconate in normal saline by nebulizer or by IPPB with 100% oxygen may decrease pulmonary damage. Bronchodilators may also be administered.

Skin: For deep skin burns or contact with concentrated HF (over 50%) solution, consider infiltration about the affected area with 5% calcium gluconate [equal parts of 10% calcium gluconate and sterile saline for injection]. Burns beneath the nail may require splitting the nail and application of calcium gluconate to the exposed nail bed. For certain burns, especially of the digits, use of intra-arterial calcium gluconate may be indicated.

Eyes: Irrigation may be facilitated by use of Morgan lens or similar ocular irrigator, using 1% aqueous calcium gluconate solution [50ml of calcium gluconate 10% in 500 ml normal saline].

AN ALTERNATIVE FIRST AID PROCEDURE: The effect of HF, *i.e.* onset of pain, particularly in dilute solutions, may not be felt for up to 24 hours. It is important, therefore, that persons using HF have immediate access to an effective antidote even when they are away from their workplace in order that first aid treatment can be commenced immediately.

We recommend that any person in contact with HF should carry, or have access to a tube of HF Antidote Gel at all times; ideally with one tube at the workplace, one on the person and one at home.

It is imperative that any person who has been contaminated by HF should seek medical advice when the treatment by HF Antidote Gel has been applied.

REFERENCES:

1. Browno, T.D. Treatment of Hydrofluoric Acid Burns
2. Sprout, W.L. et al Treatment of Severe Hydrofluoric Acid Exposures (Journal of American Occupational Medicine 25:12, 1993)
3. Bracken, W.M. et al Comparative Effectiveness of Topical Treatments for Hydrofluoric Acid Burns, University of Kansas (Journal of Occupational Medicine 27:10:1985)
4. Burke, W.J. , et al Systemic Fluoride Poisoning Resulting from A Fluoride Skin Burn (Journal of Occupational Medicine (5,39:1973)