Guidelines for the Safe Use of Hydrofluoric Acid

A. Introduction

Hydrofluoric acid (HF) has a number of physical, chemical, and toxicological properties that make it especially hazardous to handle. Both anhydrous hydrofluoric acid and aqueous solutions are clear, colorless, and corrosive liquids. When exposed to air, anhydrous HF and concentrated solutions produce pungent fumes, which are also dangerous. HF shares the corrosive properties common to mineral acids, but possesses the unique ability to cause deep tissue damage and systemic toxicity.

HF can cause more extensive DEEP TISSUE DESTRUCTION (including loss of limbs) or at a minimum, internal pain, than many common inorganic acids due to delayed awareness of exposure. Partly because HF is a relatively weak acid, it can easily penetrate the skin, bypassing typical physiological warning signs of acid exposure. Severity and timing of effects depends on the concentration, duration of exposure, and penetrability of the exposed tissue. Symptoms may start immediately or **pain may be delayed for up to 24 hours.**" Contact with aqueous solutions with concentration even <5% can cause extreme pain and tissue loss.

Prevention of exposure or injury must be the primary goal when working with HF. However, any HF user must be intimately familiar with the appropriate first aid in case of an exposure.

Please place this document inside your Chemical Hygiene Plan (CHP) binder/manual for future reference. Make sure to go over this document and your lab's own internal procedures/processes for using HF with each lab member when completing the Specific Lab Training section of your CHP manual.

<u>Requirements</u>:

To possess HF, your laboratory must meet the following requirements:

1. Have calcium gluconate gel in the laboratory in a location that is labelled and well-known to all researchers.
2. Have a spill kit labelled for use with HF
3. Have a signed "Laboratory Specific Training" document in your Chemical Hygiene Plan, signed by everyone working in the laboratory.

B. Physical Properties

Compound:	hydrofluoric acid
Synonyms:	hydrogen fluoride, fluoric acid, hydrofluoride, fluorine monohydride
CAS No:	7664-39-3
Mol. Formula:	HF
Mol. Weight:	20.01
Boiling point:	68°F (20°C) at 760 mmHg
Specific gravity:	0.99 at 19°F (-7°C)
Vapor pressure:	400 mmHg (34°F)
Vapor density:	0.7 (air=1)
pKa:	3.15

Description:	colorless gas or fuming liquid. Disagreeable, pungent odor at less than 1 ppm.
Solubility:	Miscible with water with release of heat
Flammability:	Nonflammable

C. CHEMICAL PROPERTIES

Hydrofluoric acid etches glass, due to the strong bond formed between fluoride anions and the silicon atoms in glass. HF will react violently with any glass that has a high surface area (such as glass wool). It will also react with glazes, enamels, pottery, concrete, rubber, leather, many metals (especially cast iron) and many organic compounds. Upon reaction with metals, hydrogen gas is generated that may pose an explosion hazard. HF should not be stored in steel cylinders for more than 2 years due to potential over-pressurization from hydrogen gas formation.

Many chemicals containing fluorine, such as ammonium fluoride, sodium fluoride, sulfur tetrafluoride, and ammonium bi-fluoride, may react with acid or water to produce HF. If the manner in which the fluorine compound is used can create HF, follow the precautions for HF.

D. TOXICITY

1) **Skin Contact**

HF differs from other protic acids because the fluoride ion readily penetrates the skin, causing the destruction of deep tissue layers. This process may continue for days if left untreated. Strong acid concentrations (over 50%) "cause immediate, severe, burning pain and a whitish discoloration of the skin which usually proceeds to blister formation." In contrast, the effects of more dilute solutions may be delayed. **The latency period for symptoms (redness, swelling, and blistering) to appear after exposure to aqueous HF solutions in the 20-50% range may be up to eight hours**. Solutions less than 20% may not produce symptoms for up to twenty four hours.

Fluoride ions form insoluble salts with calcium and magnesium in bodily tissue. Soluble salts can form with other cations, which dissociate rapidly causing further disruption and damage to tissue. The severe, throbbing pain associated with HF burns is thought to result from nerve irritation due to potassium cations entering the extracellular space to compensate for reduced calcium ion concentrations.

Fluoride poisoning is associated with hypocalcemia (low calcium levels), hyperkalemia (high potassium levels), hypomagnesemia (low magnesium levels), and sudden death. Systemic hypocalcemia should be considered a risk whenever skin burns from concentrated HF exceed 25 in^2 (160 cm^2), or about the size of the palm of your hand. Concentrated HF burns can be fatal if only 2% of the body surface area is exposed.

2) **Eye Contact**

HF contact with the eye can cause eye burns and destruction of the cornea. Blindness results from severe or untreated exposures.

3) **Inhalation**
Inhalation of HF vapors may cause "laryngospasm, laryngeal edema, bronchospasm and/or acute pulmonary edema." The symptoms of exposure are coughing, choking, chest tightness, chills, fever, and blue skin.

The Permissible Exposure Limit (PEL) set by the U.S. Occupational Safety and Health Administration (OSHA) is a time weighted average exposure for 8 hours of 3 ppm. The National Institute for Occupational Safety and Health (NIOSH) has set the Immediately Dangerous to Life and Health (IDLH) level at 30 ppm (30 min).

4) **Ingestion**
Severe burns to the mouth, esophagus, and stomach may occur upon ingestion of HF. The ingestion of a small amount of HF has resulted in death.

5) **Chronic Toxicity**
HF has not been studied for chronic toxicity, in part due to the fact that it is such a strong irritant. There are studies that examine the chronic toxicity from long-term, high exposure to fluoride salts.

E. WORKING WITH HYDROFLUORIC ACID

1) **Preparation**
Before any researcher uses HF, they should do the following:

- Read a SDS for HF.
- Read this document and consult the references below.
- Review or create a Standard Operating Procedure (SOP) for the process in which HF is used, incorporating information contained in this document.
- Know the first aid procedure in case of exposure
- Know what to do in case of a spill.
- Contact the UK EHS: Occupational Health & Safety (Lee Poore – 859-257-2924) and/or College Safety Officer (Jay Young – 859-257-7728) with questions.

2) **Designated Area**

- HF should always be handled inside of a fume hood which is identified with a sign stating "Danger, Hydrofluoric Acid Used in this Area."
- The SOP should be posted or readily available near the designated area.
- First Aid
    - a tube of 2.5% calcium gluconate gel (consider several tubes if large volumes of HF are present) ***must*** be present.
    - the gel should be replaced annually (or at the expiration date of the tube)
- An HF spill kit should be nearby.
- Ensure you have ready access to a good supply of running water and know the location of the safety shower and eyewash (include as part of SOP).

3) **Personal Protective Clothing**
When using HF, you must wear protective clothing:

- Laboratory coat

- Close-toed shoes and long pants
- Goggles or full-face shield in conjunction with goggles
- Gloves
    - nitrile exam gloves (consider double gloving) for brief use of dilute solutions
    - heavy nitrile or neoprene gloves for concentrated solutions or extended use of any solution
    - check the gloves for leaks by inflating the glove and then closing the cuff. An intact glove should hold air (you may also submerged in water and look for bubbles).

4) **Safe Laboratory Practices**

- Never work alone or after hours with HF.
- HF reacts with glass, which should never be used to store or transfer it. Use chemically compatible containers, such as those made from polyethylene or Teflon.
- Ensure all containers of HF are clearly labeled, including concentration.
- Always work with a chemically compatible secondary containment tray (e.g. polyethylene or Teflon).
    - Glass, metal, or ceramic containers are **NOT** compatible with HF
- Ensure HF containing vials and flasks are securely supported and not likely to tip over.
- Keep containers closed to minimize exposure and prevent etching of fume hood glass from HF vapors.

5) **Transporting HF**

If an HF containing solution must be transported from one lab area to another:

- Place the object in a clean, chemically compatible container and close the lid.
- Remove your gloves before transporting the container to avoid the possibility of chemical contamination on your gloves spreading to door handles and other objects.
    - Or consider putting on a single clean glove with which to carry the container, leaving an ungloved hand to open doors and handle other objects.
    - Or have a lab member open doors and handle objects for you.

6) **Managing HF Containing Waste**

- HF that is hazardous waste should be placed in a chemically compatible container that is clearly labeled with a Hazardous Waste label/sleeve and that is compliant with all university hazardous waste container policies (e.g. contents listed, secure/closed cap, no date until submitted for pickup, etc.).
- Dispose of HF containing hazardous waste containers following the regular Etrax hazardous waste disposal procedure.
- Insure that any container of HF containing material is marked with **clearly visible marking** to indicate there is HF present.
- Contact UK EHS: Environmental Management (323-6280) and/or College Safety Officer (Jay Young – 859-257-7728) with questions.

F. FIRST AID

Often symptoms of HF exposure are delayed for several hours after exposure. If you suspect you may have been exposed to HF, but do not experience any immediate symptoms, apply immediate first aid anyway. A quick response can substantially reduce injury. No person exposed to HF should be allowed to go home or return to work without having seen a doctor who is aware of the nature and extent of the exposure.

Skin

1. Immediately proceed to the nearest wash station/safety shower and wash the contaminated area with copious amounts of running water for 15minutes. Speed and thoroughness in washing off the acid is essential.
2. Remove all contaminated clothing while rinsing.
3. While washing the affected area, have someone call 911 for emergency medical assistance.
4. Continuously massage calcium gluconate gel (HF First aid kit) gently on and around the area of concern with gloved fingers (to prevent possible secondary HF burns). The gel will turn white (CaF_2 precipitate) upon reaction with the acid. If calcium gluconate gel is not available, rinsing must continue.
5. Continue application of calcium gluconate until further medical treatment is available.
6. Proceed to a physician for appropriate follow-up and/or treatment. Take calcium gluconate gel and HF SDS or concentration information (have lab member help with this if possible) with you.

Eyes

1. Immediately flush the eyes with water, preferably at an eyewash station for at least 15 minutes. Gently hold the eyelids away from the eye to fully irrigate the eye.
2. Do not apply 2.5% calcium gluconate gel to the eye.
3. While washing the eye, have someone call 911 for emergency medical assistance.
4. Flushing can be limited to five minutes if medical personnel are immediately available to administer sterile calcium gluconate (1%) solution (via continuous drip into eyes).
5. Proceed to a physician for appropriate follow-up and/or treatment.

Inhalation of Vapors

1. Immediately move affected person to fresh air and call 911 for medical assistance.
2. Keep victim warm, comfortable and quiet.
3. If breathing has stopped, start artificial respiration at once (if CPR/First Aid certified).
4. Oxygen should be administered as soon as possible by medical personnel.
5. Proceed to a physician for appropriate follow-up and/or treatment.

Ingestion

1. Have the victim drink large amounts of room temperature water as quickly as possible to dilute the acid. Do not induce vomiting. Do not give anything by mouth to an unconscious person.
2. Call 911 for medical assistance.

3. Give several glasses of milk or several ounces of milk of magnesia, Mylanta, Maalox, or antacid tablets with water. The calcium or magnesium salts in these substances may act as an antidote. Avoid administering bicarbonates at all costs; the carbon dioxide byproduct could severely injure the victim.
4. Proceed to a physician for appropriate follow-up and/or treatment.

G. HYDROFLUORIC ACID SPILLS

Follow the regular guidelines for chemical spills in the lab: http://stockroom.chem.uky.edu/node/40

If uncomfortable cleaning up the spill on your own, please follow the chemical spill procedure and contact UK Environmental Management (859-323-6280) or UK Police dispatch (859-257-8573) after hours.

Procedure:

1. Immediately alert others working in the area. Notify supervisor and evacuate the area if necessary.
2. If there is a threat of fire, injury or environmental release, CALL 911.
3. Attend to any individual who may be contaminated. Clothing and jewelry need to be removed and skin flushed for a minimum of fifteen minutes.
4. If the spill involves a flammable material, immediately control sources of ignition and ventilate the area.
5. Don appropriate personal protective equipment.
6. If the spill is major (more than 1 gallon or 4 liters), or if assistance is needed call Environmental Management (EM) at 323-6280 or UK Police Dispatch at 257-8573 after hours.
7. Protect floor drains or other avenues of environmental release.
8. When spilled materials have been absorbed, place materials in appropriate container and fill out an E-trax hazardous waste card.
9. The container can be placed in fume hood for proper ventilation until pickup by EMD personnel.
10. The area should be decontaminated with a mild detergent and water and cleared by EMD and OHS personnel before work resumes.
11. No PPE should be removed until the spill is completely cleaned up.

If a minor spill occurs (100 ml or less) and you feel that you and your lab-mates are capable of addressing the spill, follow the Chemical Spill Procedure with the following modifications:

- Only HF specific absorbents should be used to address an HF spill. Typical spill absorbents contain silica, which can react with HF to produce the toxic gas silicon tetrafluoride.
    - calcium carbonate or calcium hydroxide for spill absorbent
        - or commercial HF spill kit
- Obtain a HF spill kit from your lab.
- Carefully address the spill using the HF spill kit.

- Notify the College Safety Officer (Jay Young – 859-257-7728) and UK EHS: Environmental Management (323-6280)

H. REFERENCES

Recommended Medical Treatment for Hydrofluoric Acid Exposure, Honeywell (Industrial Fluorines), May 2000. (An informational and medical guide prepared by the largest industrial producer of hydrofluoric acid). www.hfacid.com (checked March 2007)

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Guidelines For Using Hydrofluoric Acid, Desert Research Institute, Novermber 2004, http://safety.dri.edu/Hazards/HydrofluoricAcidGuidelines.pdf (checked August 2006)