Guidelines for the Safe Use of Hydrofluoric Acid

1. 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 highly corrosive liquids. All forms including the solution or the vapor can cause severe burns to tissue which are very painful and very slow to heal. 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. 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.

**WARNING:** BURNS WITH CONCENTRATED HYDROFLUORIC ACID (HF) ARE USUALLY VERY SERIOUS, WITH THE POTENTIAL FOR SIGNIFICANT COMPLICATIONS DUE TO FLUORIDE TOXICITY. CONCENTRATED HF, LIQUID OR VAPOR, MAY CAUSE SEVERE BURNS, METABOLIC IMBALANCES, PULMONARY EDEMA AND LIFE THREATENING CARDIAC ARRYTHMIAS. EVEN MODERATE EXPOSURES TO CONCENTRATED HF MAY RAPIDLY PROGRESS TO FATALITY IF LEFT UNTREATED

2. Chemical Properties:

Hydrofluoric acid etches glass, due to the strong bond formed between fluoride anions and the silicon molecules in glass. 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. HF cannot be stored in glass bottles.
3. Toxicity and Health Hazards:

HF exposures are considered among the most hazardous to human health when they occur; this is due to the lack of immediate physical warning symptoms related to exposure. However, delayed symptoms after only slight or short duration exposures often arrive after significant internal damage has already begun to occur. For this reason, all real or potential exposures to HF must be taken very seriously by anyone who either works with or is in the vicinity where work with HF liquids will occur.

HF differs from other protic acids because the fluoride ion is readily absorbed through intact healthy skin and can easily make its way into the bloodstream, causing the destruction of deep tissue layers. This process may continue for days if left untreated. Fluoride ions are both acutely and chronically toxic. Acute effects of HF exposure include extreme respiratory irritation, immediate and severe eye damage and pulmonary edema. Skin, eye, or lung exposure to concentrated (>50%) HF solutions will cause immediate, severe, penetrating burns and a whitish discoloration of the skin which usually proceeds to blister formation. Exposure to less concentrated solutions may have equally serious effects, but the appearance of symptoms can be delayed up to 24 hours. If you are exposed to hydrofluoric acid seek medical attention immediately, even if you do not feel pain. Fluoride poisoning is associated with hypocalcemia (low calcium levels), hyperkalemia (high potassium levels), hypomagnesemia (low magnesium levels), and sudden death. Systemic hypoclcemia should be considered a risk whenever skin burns from concentrated HF exceed 160 cm$^2$, or about the size of the palm of your hand. Concentrated HF burns can be fatal if only 1% of the body surface area is exposed.

HF exposures require immediate and specialized first aid and medical treatment. Delays in first aid care or medical treatment or improper medical treatment will likely result in greater damage or may, in some cases, result in a fatal outcome.

**Skin Contact:** HF readily penetrates human skin, allowing it to destroy and decalcify soft tissues and bone. As little as a single drop of HF from a pin hole in a chemical glove has lead to the exposed finger tip having to be amputated

**Eye Contact:** Eye exposure to HF may result in severe eye burns with destruction or clouding of the cornea. Blindness or permanent eye damage may result if untreated.

**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. Delayed reactions up to and including fatal pulmonary oedema (flooding of the lungs with body fluids) may not be apparent for hours after the initial exposure.

**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

4. Working with HF

Prior to conducting any work with HF the Principal Investigator must provide training to all laboratory personnel in his/her laboratory specific to the hazards involved with this substance, work area decontamination, and first aid and emergency procedures.
At a minimum, the training program shall consist of the following topics:

- A description of the hazards associated with HF
- A description of the initial first aid measures
- A description of the delayed onset of symptoms associated with HF
- A description of the personal protective equipment available and a description of its use and limitations
- The location of Material Safety Data Sheets and other safety, health & environmental information
- The location of first aid equipment on site
- The correct response to involvement in an HF incident
- Emergency procedures, including how to contact Security (585-4999)
- How/where to get medical attention (calling 911 in an emergency)
- The importance of cleaning up and decontaminating surfaces and equipment when work is complete (contact HSE: health.safety@uregina.ca for more information)
- The importance of labeling samples or contaminated equipment
- The importance of reporting all incidents or near misses so that recurrences are prevented. All incidents and near-misses should be reported to HSE (health.safety@uregina.ca)
- A practical demonstration showing how to put the personal protective equipment on (See section on PPE)
- A practical demonstration of the decontamination procedures (site specific procedures need to be developed for each lab/experiment)
- A practical demonstration of the use of calcium gluconate gel
- Validation of the understanding of each part of the procedure the PI and/or HSE should observe a dry-run of the experiment prior to any work being performed with HF
- A check that each attendee has a tube of calcium gluconate gel available at home
- The importance of reporting any exposure, either while at work or home (any exposure should be immediately treated and reported to HSE)

**Antidote:** The Principal Investigator must ensure that an adequate supply of 2.5% calcium gluconate gel (within expiration date) is available and all staff is aware of its location. It is suggested that anyone using HF, or who could possibly come into accidental contact with it (e.g. people working in the same laboratory or regular visitors), keep a fresh tube of gel at home at all times.

**Storage:** HF should be stored in a location that is secure to unauthorized access. Examples are a locked cabinet, or within a laboratory that is locked when authorized personnel are not present. A cabinet containing HF must be labeled with a caution sign noting the presence of HF and its hazards (contact HSE for help in creating signs). Store HF in appropriate, chemically compatible (no glass or metal) sealed containers within unbreakable, compatible secondary containment (i.e., a polyethylene tub or tray)

**Work Practices:**

- HF should always be handled in a **designated area** such as inside a chemical fumehood which is identified with a sign stating “Danger, Hydrofluoric Acid Used in this Area”
- Copies of MSDS and these guidelines should be posted or readily available near the designated area
- An HF spill kit should be nearby, it is recommended that “HF Acid Eater” be a part of the spill kit
- A HF Exposure Kit should be available and contain the following items:
  - A tube of 2.5 calcium gluconate gel. The gel must be inspected at least monthly to ensure that it is available and has not reached the expiration date. If the gel has exceeded its shelf life or has been opened, a new tube must be purchased and the old tube discarded.
  - 2 pairs of Neoprene or Nitrile (minimum 22 mil) gloves
  - 1 heavy duty polyethylene bag to be used for items contaminated by HF
• Copy of these guidelines and MSDS to take to the emergency room
• Calcium Carbonate (antacid tablets) within expiration date
• HF should be purchased in the smallest amount, and in no instance should the bottle size exceed 500mL
• It must not be heated. When heated, highly corrosive HF vapor is emitted. Facilities Management must determine if the fume hood is suitable for the specific HF use required by the experiment.
• A minimum of two individuals trained in the hazards of HF must be present whenever HF is used. Each individual must be familiar with the applicable first aid procedures, maintain visual contact with the other, and be ready to assist in the event of an incident
• Never use HF working alone or after hours
• HF must be opened and handled only in a chemical fume hood, bench top use of HF is prohibited. The fume hood sash should be lowered to operating height or below. Containers of HF must not be left open since vapors can etch the glass of the hood sash.
• Do not use glass lab ware for work with HF.
• Wash hands thoroughly immediately after working with any concentration of HF.

Personal Protective Equipment:
• Splash-proof chemical goggles with plastic face shield (available from Science Stores)
• Neoprene gloves over nitrile gloves. Double-gloving is required when working with HF. Inspect gloves frequently and replace immediately if punctured or torn. If neoprene gloves are to be reused, rinse thoroughly with water and dip into a saturated solution of calcium carbonate
• Full-length lab coat with a chemical-resistant apron over top
• Closed-toe, preferably leather shoes (not fabric or mesh) or boots made of polyvinyl alcohol (PVA)

5. First Aid Procedures:
HF exposure requires immediate and specialized first aid and medical treatment. Prompt first aid is essential even if the victim does not exhibit any signs or symptoms, or feel any pain. First aid should be initiated if any contact is suspected because burns from weak HF solutions may not be noticed immediately. First aid must be followed by treatment by a physician as soon as possible.

Skin contact:
1. Immediately proceed to the nearest safety shower & wash the contaminated area with copious amounts of running water for a minimum of 5 minutes (if calcium gluconate gel is available, otherwise run the shower for 15 min). Speed and thoroughness is washing off the acid is essential. Remove all contaminated clothing while rinsing
2. While the victim is rinsing the affected area, someone should call 911 and Campus Security (585-4999)
3. After rinsing, victim should apply calcium gluconate gel and massage into the contact site and adjacent area, while wearing protective gloves. If assistance is required in applying the gel, the person assisting should wear gloves to avoid a secondary burn. Apply gel frequently (every 15 minutes) and continually massage into skin. Continue until at least 15 minutes after pain is relieved or until medical treatment is provided. Continue applying gel during transport to a medical facility. The gel will turn white upon reaction with the acid.

Eye contact:
1. If HF liquid or vapor has contacted the eyes, immediately flush for at least 15-20 minutes. Hold upper and lower eyelids open and away from the eye during irrigation.
2. Do not apply calcium gluconate gel to the eye.
3. While the victim is rinsing, someone should call 911 and Campus Security (585-4999).
4. Remove contact lenses if possible. Continue flushing with an eyewash or apply ice water compresses during transport to medical facility or eye specialist.

5. Avoid rubbing of the eyes.

6. Proceed immediately to a physician for appropriate follow-up treatment

**Inhalation:**
1. Vapour exposures can cause skin and mucous membrane burns as well as damage to pulmonary tissue
2. Immediately move the victim to fresh air and call 911 and Campus Security (585-4999)
3. Keep victim warm, comfortable and quiet
4. Oxygen should be administered as soon as possible by medical personnel

**Ingestion:**
1. Have victim drink large amounts of room temperature water as quickly as possible to dilute the acid.
2. Drink several glasses of milk or several ounces of Mylanta, Maalox of milk of magnesia, or antacid tablets (all contain calcium or magnesium which may act as an antidote).
3. Do not induce vomiting, do not give emetics or baking soda or any bicarbonates, the carbon dioxide byproduct could severely injure the victim
4. Do not give anything by mouth to an unconscious person
5. Call 911 and Campus Security (585-4999)
6. Obtain immediate medical attention. Ingestion of HF is a life-threatening emergency

_In all cases of exposure, you must bring a copy of the MSDS; the emergency room physician may not be aware of the specific treatment measures for HF_

**6. Spill Procedures**

If **HF is spilled outside of a chemical fume hood**: Evacuate the area and close the doors. Post a sign to ensure others do not enter the area. Call Campus Security and HSE. Do not call 911, HSE and the Spill Response Team is best equipped to deal with an HF spill.

If **HF is spilled in a fume hood**: The spill may be cleaned up by laboratory staff if they have the correct equipment, understand the hazards, know how to clean up the spill safely and only if they feel comfortable doing so. HSE should be notified prior to any clean-up procedure.

- Only HF-specific absorbents should be used to address an HF spill. Do not use typical spill absorbents (SPILL-X, kitty litter, sand or Floor-dri) as they contain silica, which can react with HF to produce the toxic gas silicon tetrafluoride.
- Lime, soda ash, calcium carbonate or calcium hydroxide should be kept nearby to use in case of a spill
- Add neutralizers slowly, as the reaction can be vigorous

**7. Decontamination and Waste Disposal**

- Waste HF should be placed in a chemically compatible container that is clearly labelled
- Contact HSE (health.safety@uregina.ca) to arrange for a waste disposal drop off