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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 highly 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.

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.

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 molecules in glass. HF will also react with glazes, enamels, pottery, concrete, rubber, leather, many metals (especially cast iron) and many organic compounds. Hydrogen gas, which may pose an explosion hazard, is generated upon reaction with metals. HF should not be stored in steel cylinders for more than 2 years due to potential over-pressurization from hydrogen gas formation.

"Many fluoride-containing chemicals (e.g. 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 fluoride 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 the body surface area of 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 an MSDS for HF.
- Read this document and consult the references below.
- Review or create a Standard Operating Proceedure (SOP) for the process in which HF is used, incorporating information contained in this document.
- Obtain a Calgonate first aid kit from the CCB Safety Office and review the first aid procedures therein.

- Obtain a Calgonate spill kit from the Safety Office and review the procedures to follow in the event of a spill.

- Contact the CCB Safety Office (Mathieu Lalonde, lalonde@fas.harvard.edu, 496-8285) with any questions.

2) **Designated Area**

- HF should always be handled inside of a fume hood that 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) or Zephiran solution must be present. Each Calgonate first aid kit contains two tubes of 2.5% calcium gluconate gel.
  - The gel should be replaced annually (the expiration date is clearly marked on 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.

3) **Personal Protective Clothing**

When using HF, you must wear protective clothing:

- Laboratory coat and acid resistant apron.
- Close-toed shoes and long pants.
- Goggles or full-face shield in conjunction with goggles.
- Gloves
  - **Brief use of dilute solutions:** nitrile exam gloves can be employed. Consider double gloving. **Nitrile rubber gloves are not recommended for handling ≥30% HF.**
  - **For the use of concentrated solutions:** use gloves that cover the hands, wrists, and forearms. According to the Quick Selection Guide to Chemical Protective Clothing (5th edition, page 149), the following gloves will provide protection from hydrofluoric acid (30-70%) for 4 hours or more: Butyl rubber, neoprene rubber, Viton®/butyl rubber, Barrier® (PE/PA/PE), Silver Shield/4H® (PE/EVAL/PE), Trellchem® HPS, Trellchem® VPS, Tychem® SL (Saranex®), Tychem® CPF3, Tychem® BR/LV, Tychem® Responder®, Tychem® TK.

  - The following gloves will protect against hydrofluoric acid (>70%) for 4 hours or more: Neoprene rubber, Barrier® (PE/PA/PE), Trellchem® HPS, Tychem® TK

4) **Safe Laboratory Practices**

- Never work with HF alone or after hours.
- 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.
- Always work with a chemically compatible secondary containment tray.
- 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 labmate open doors and handle objects for you.

6) **Managing HF Containing Waste**

- Waste HF should be placed in a chemically compatible container that is clearly labeled with a Hazardous Waste tag and that is compliant with all Harvard waste container policies (e.g. secondary containment, closed cap, etc.).
- Dispose of HF containing hazardous waste containers following the usual hazardous waste disposal procedures.
- Contact Harvard Environmental Health and Safety (EHS) with questions (495-2060).

F. First Aid

Symptoms of HF exposure are often delayed for several hours. If you suspect you may have been exposed to HF but are not experiencing any immediate symptoms, apply immediate first aid nonetheless. 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.

Prevent cross contamination: the victim of HF exposure should perform the following actions on him/herself whenever possible. Anyone who provides assistance should use the proper gloves, and other personal protective equipment mentioned in this document, in order to prevent contaminating themselves. **Do not use latex gloves**; they do not provide an effective barrier against chemicals, especially HF.

Emergency personnel responding to an HF exposure should be informed not to administer painkillers. Unfortunately, one of the telltale signs that HF has been "titrated" from the body is the disappearance of pain. The inability to feel pain prevents the patient from knowing whtehr or not the treatment was sufficient.

Skin exposure:

1) Immediately flush affected areas with cold running water (shower if available). While flushing, remove all contaminated clothing as well as jewelry that could trap HF. Wash the contaminated area with copious amounts of running water for 5 minutes. Speed and thoroughness in washing off the acid is essential. If calcium gluconate gel (2.5%) is not available, continue flushing with water for at least 15 minutes or until medical treatment is given.

2) While the victim is being rinsed with water, someone call 911 and say (a) a person has been exposed to hydrofluoric acid. (b) The person can be found at [give location of victim]. (c) Please send an ambulance.

3) Don a new pair of chemical resistant gloves (to prevent possible secondary HF burns) and massage calcium gluconate gel (2.5%) freely into the affected site. Apply the gel as soon as the washing is done. The affected area does not need to be dried first. The gel will turn white (CaF_2 precipitate) upon reaction with the acid.

OR

Soak the affected area in, or apply compresses of, iced Zephiran solution (a 0.13% aqueous solution of benzalkonium chloride).

4) After these actions have begun, re-examine the victim to ensure no exposure/burn sites have been overlooked.

5) Calcium gluconate gel (2.5%) should be re-applied, or Zephiran soaking repeated, every 10-15 minutes until the ambulance arrives or a physician/EMT gives medical treatment.

6) Provide the following information to the EMS team, and/or physician: (a) The concentration of the hydrofluoric acid and its MSDS. (b) Date, time of exposure, duration of exposure, and how exposure occurred. (c) Body parts affected or exposed, and the percent of body surface area affected. (d) Summary of first aid measure given, including when calcium gluconate gel or Zephiran was first applied, the body areas to which the treatment was applied, and how many times the treatment was applied in total.

Eye exposure:

1) Immediately flush eyes with cool flowing water, preferably at an eyewash station, or sterile eyewash solution. Hold the eyelids open and away from the eye during irrigation to allow thorough flushing of the eyes. If sterile 1% calcium gluconate solution is available, start using it within the first 5 minutes (via continuous drip into eyes), and continue using it as the preferred flushing agent (Do NOT use 2.5% calcium gluconate GEL on the eyes). If sterile 1% calcium gluconate solution is not available, wash with copious amounts of water for 15 minutes while holding eyelids apart.

2) While washing the eye, have someone call 911 for emergency medical assistance, preferably an eye specialist. Calcium gluconate solution (1%), eyewash, clean water, or ice water compresses should be used to continue to irrigate the eye(s) while transporting the victim.

<u>Inhalation of Vapors</u>

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, begin CPR at once. Make sure mouth and throat are free of foreign material.

4) 100% oxygen (10 to 12 L/min flow rate) should be administered as soon as possible by a trained individual.

5) A nebulized solution of 2.5% calcium gluconate may be administered with oxygen by inhalation.

6) Do not give stimulants unless instructed to do so by a physician.

7) The victim should be examined by a doctor and held for observation for at least 24 hours. The reason is that inhalation of HF fumes may cause swelling in the respiratory tract up to 24 hours after exposure. A person who has inhaled HF vapors may require prophylactic oxygen treatment. Vapor exposure can cause skin and mucous membrane burns and damage to pulmonary tissue. Vapor burns to the skin are treated the same as liquid HF burns.

Ingestion:

1) Do not induce vomiting. Never give anything by mouth to an unconscious person.

2) Have the victim drink large amounts of room temperature water as quickly as possible to dilute the acid.

3) Call 911 for medical assistance.

4) Have the victim drink several glasses of milk or several ounces of milk of magnesia, Mylanta, Maalox or similar products, or eat up to 30 Tums, Caltrate or other antacid tablets. The calcium or magnesium in these substances may act as an antidote. Avoid administering bicarbonates at all costs, the carbon dioxide byproduct could severely injure the victim.

5) Proceed to a physician for appropriate follow-up and/or treatment.

G. Hydrofluoric Acid Spills

Read the "CCB Chemical Spill Policy" available on the CCB Safety Website (www.chem.harvard.edu/safety/labsafety.php). This document provides criteria to assist in determining when a chemical spill can be addressed by local researchers (minor spills) or when outside help is required (major spills). It also offers guidance on how to cleanup a minor spill. No researcher is responsible for addressing a spill themselves if they are not comfortable doing so, even if the spill meets the characteristics of a "minor" one.

If a major HF spill occurs, follow the Major Spill Protocol described in the CCB Chemical Spill Policy:

1) Alert nearby coworkers and evacuate to a safe distance.
2) If a fire, explosion, or toxicity hazard exists, pull the fire alarm and follow building evacuation procedures. A person familiar with the situation should greet firefighters on Oxford Street when they arrive and provide the relevant material safety data sheets (MSDS) or safety data sheets (SDS).
3) If you have not pulled the fire alarm, close doors of affected areas and prevent re-entry. Put up "Do Not Enter" signs or barrier tape (available outside CCB Safety Office and in HF spill kit).
4) Call the Operations Center at **5-5560** to obtain assistance (they will contact EH&S, Triumvirate, and/or the Fire Department). Call the CCB Safety Office at **6-8285** to inform them of the situation.

5) Do not re-enter the area until instructed to do so by the Fire Department or emergency response personnel.

If a minor spill occurs and you feel that you and your lab-mates are capable of addressing the spill, follow the Minor Spill Protocol with the following modifications:

• Notify the CCB Safety Office. The CCB Science Safety Officer can assist with the cleanup.

• Obtain a HF spill kit from your lab or from outside of the CCB Safety Office and employ the HF neutralizer found therein. Only HF specific absorbents should be used to address an HF spill. If such absorbents are not available, a large excess of dilute, aqueous calcium or magnesium hydroxide can be employed. The neutralization should be performed slowly in order to avoid an exothermic reaction (heat will vaporize HF and increase the risk of exposure).

Do not attempt to neutralize HF with the following:

1) Sodium or Potassium Carbonate ("Soda Ash", "Caustic Soda"): The reaction of Na_2CO_3 or K_2CO_3 with HF generates sodium or potassium hydrogen bifluoride ($NaHF_2$ or KHF_2) as intermediates, which release gaseous HF when exposed to heat.

2) Potassium or Sodium Hydroxide (found in many acid-neutralizing kits): The neutralization of HF with potassium or sodium hydroxide is more exothermic than with sodium or potassium carbonate and also generates potassium or sodium hydrogen bifluoride ($NaHF_2$ or KHF_2) as intermediates, which release gaseous HF when exposed to heat.

3) Silicon-based absorbent materials (common in most solvent spill kits) react with HF to generate silicon tetrafluoride, which is a toxic and corrosive gas.

H. References

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