



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

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| <i>Compound:</i> | hydrofluoric acid |
| <i>Synonyms:</i> | hydrogen fluoride, fluoric acid, hydrofluoride, fluorine monohydride |
| <i>CAS No:</i> | 7664-39-3 |
| <i>Mol. Formula:</i> | HF |
| <i>Mol. Weight:</i> | 20.01 |
| <i>Boiling point:</i> | 68°F (20°C) at 760 mmHg |
| <i>Specific gravity:</i> | 0.99 at 19°F (-7°C) |
| <i>Vapor pressure:</i> | 400 mmHg (34°F) |
| <i>Vapor density:</i> | 0.7 (air=1) |
| <i>pKa:</i> | 3.15 |
| <i>Description:</i> | colorless gas or fuming liquid. Disagreeable, pungent odor at less than 1 ppm. |
| <i>Solubility:</i> | Miscible with water with release of heat |
| <i>Flammability:</i> | Nonflammable |

C. 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.

“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 in² (160 cm²), 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 Procedure (SOP) for the process in which HF is used, incorporating information contained in this document.
- Know the first aid procedure in case of
- Know what to do in case of a spill.
- Contact the CCB Safety Office (Allen Aloise, aloise@fas.harvard.edu, 496-8285) 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) or Zephiran solution must be present.
 - the gel should be replaced annually
- 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
 - 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

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.
- 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

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 5 minutes. 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 (available in the VWR stockroom) gently on and around the area of concern with gloved fingers (to prevent a 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.

OR

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

- 5) Continue application of calcium gluconate gel or Zephiran soaking until further medical treatment is available.
- 6) Proceed to a physician for appropriate follow-up and/or treatment. Take calcium gluconate gel with you.

Eyes

- 1) Immediately flush the eyes with water, preferably at an eyewash 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).
- 4) 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.
- 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.
- 2) Give several glasses of milk or several ounces of milk of magnesia, Mylanta, Maalox, or antacid tablets with water. 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.
- 4) 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 evaluating when a chemical spill can be addressed by local researchers (minor spills) and when outside help is necessary (major spills). It also offers guidance on how to clean-up 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 MSDSs.
- 3) If you have not pulled the fire alarm, close doors to affected areas and prevent re-entry. Put up Do Not Enter signs or barrier tape (available outside CCB Safety Office).
- 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:

- 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.
- Obtain a HF spill kit from your lab or from outside of the CCB Safety Office.
- Carefully address the spill using the HF spill kit.
- Notify the CCB Safety Office.

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).

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Guidelines for the Safe Use of Hydrofluoric Acid, University of Pittsburgh, September 2005,

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