Hydrofluoric Acid and Lipophilic Fluorinated Agents
SOP

Summary
The purpose of this SOP is to ensure the proper management and to minimize exposures to and accidental releases of hydrofluoric acid, and other compounds capable of liberating HF or which can present similar hazards.

This procedure applies to all personnel who handle hydrofluoric acid on the University of Massachusetts, Amherst, campus and its research stations.

What is hydrofluoric acid?
Hydrofluoric acid (HF) is a weak inorganic and extremely corrosive acid used for many purposes including mineral digestion, surface cleaning, etching, metal cleaning, and as a laboratory reagent. HF can be found in some household products such as rust removers, automotive detailing products, and stain removers. The unique properties of HF make it significantly more hazardous than many of the other acids used on campus.

Chemical Properties:
- Clear, colorless liquid
- Density 1.15
- VP=25 mm Hg
- BP=108°C
- Melting point = -36°C
- Acrid, pungent Odor (Odor threshold = 0.04 ppm)
- Distinct ability to dissolve glass
- May form explosive levels of hydrogen upon contact with metals
- Will dissolve glazes, enamels, pottery, concrete, and leather
- Incompatible with metals and alkali

Exposure Limits
- ACGIH TLV (8 hour TWA) = 0.5 ppm
- ACGIH TLV (Ceiling) = 2 ppm
- NIOSH IDLH = 30 ppm
Responsible Persons

Principle Investigator and personnel under his/her supervision. The Principle Investigator is responsible for training students and staff in the proper handling of HF and on the use of personal protective equipment. All activities involving the use of HF should follow written protocols that have been approved by the Institutional Chemical Safety Committee (ICSC).

Safety Precautions for Handling and Storage of HF

Safe Work Practices

Do not work alone when you are using HF. Do not eat, smoke, or drink where HF is handled. Do not have exposed skin. Wash hands thoroughly after handling HF. All procedures involving HF must be designed to minimize the potential for any contact, and must be approved by the ICSC before any work with HF can take place.

Storage

Store all HF and HF waste in labeled chemically compatible containers (e.g., polyethylene or Teflon). Glass, metal, and ceramic containers are not compatible with HF. HF should never be stored with incompatible chemicals such as ammonia or other alkaline materials. Always place HF on a low protected shelf or other location where it will not be accidentally spilled or knocked over. Use secondary containment. HF containers which have become brittle must be referred for collection as hazardous waste.

Waste Handling

HF waste should be placed in a chemically compatible container (i.e., polyethylene or Teflon) with a sealed lid and clearly labeled. Complete a hazardous waste label, affix the label to the container, and submit a pickup request through CEMS. Call Environmental Health and Safety at 545-2682 for a hazardous waste label or for any questions regarding the disposal of HF waste.

Hazards Associated with Other Fluorine Compounds

Many inorganic compounds containing fluorine, such as ammonium fluoride, sodium fluoride, sulfur tetrafluoride, and ammonium bifluoride, may react with acid to produce HF. Other fluoroorganic compounds, including most nucleophilic fluorinating reagents and sulfonyl fluorides, may react with water or other compounds to release HF, or present sources of lipophilic fluoride. Review the SDS of all fluorine containing compounds carefully for safety. If the manner in which the fluorine compound is used can create HF, or other sources of fluoride capable of deep tissue penetration, follow the precautions for HF and keep topical antidote on hand. Contact EH&S for questions about specific compounds and procedures. Some common examples of materials which might be of concern include, but are not limited to:

- Pyridine hydrofluoride (Olah’s Reagent)
- (Diethylamino)sulfur trifluoride (DAST)
- 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone hydrofluoride (DMPU-HF Reagent)
- (Diethylamino)difluorosulfonium tetrafluoroborate (XtalFluor-E)
- Difluoro(morpholino)sulfonium tetrafluoroborate (XtalFluor-M)
• 2-pyridinesulfonyl fluoride (PyFluor)
• Triethylamine trihydrofluoride (TREAT-HF)
• SuFEx click reagents

**How Can Exposures and Physical Hazards Be Minimized?**

When working with any hazardous material or process, always conduct a thorough risk assessment and employ the hierarchy of controls to minimize risk. Some specific applications of the hierarchy of controls to the unique hazards of hydrofluoric acid and fluorinating agents are listed below. Always apply the controls in the order of most effective to least effective (see graphic), and apply as many controls as possible to reduce the risk to the lowest achievable level.

**Elimination/Substitution**
- Choose a less hazardous material if possible.

**Engineering Controls**
- **Ventilation:** HF should be used with adequate ventilation to minimize the inhalation of vapor. All solutions of HF should always be handled inside a properly functioning chemical fume hood. Always check the flow controller on the fume hood to ensure adequate face velocity of air entering the unit. The chemical fume hood needs to have a current calibration sticker (within 1 year). If the calibration is out of date, or if there are performance issues with a fume hood, report these to the physical plant: [https://www.umass.edu/af-forms/physicalplant/service-request](https://www.umass.edu/af-forms/physicalplant/service-request).

**Administrative Controls**
- All procedures involving HF must be designed to minimize the potential for any contact, and must be approved by the ICSC before any work with HF can take place.
- Do not work alone when you are using HF.
- Do not eat, smoke, or drink where HF is handled.
- Store all HF and HF waste in labeled chemically compatible containers and use secondary containment.
- Always place HF on a low protected shelf or other location where it will not be accidentally spilled or knocked over.

**Personal Protective Equipment (PPE)**
- **Eye Protection:** Always use ANSI z 87.1+ approved chemical splash goggles together with a face shield when handling concentrated HF. Safety glasses with side shields do not provide adequate eye protection due to HF’s highly corrosive nature.
**Body Protection:** Wear a laboratory coat with a chemical splash apron made out of natural rubber, neoprene, or Viton. *Never wear shorts or open-toed shoes when handling HF or any hazardous material.*

**Gloves:** Typically medium or heavyweight Viton, nitrile, or natural rubber gloves are worn when working with HF. Always consult the manufacturer’s glove selection guide when selecting a glove for HF. A second pair of nitrile gloves should be worn under the gloves for protection against leaks. Gloves that have not been contaminated with HF may be disposed of in the common trash. If gloves become contaminated with HF, remove them immediately, thoroughly wash your hands, and check your hands for any sign of contamination. Contaminated gloves must be disposed of as HF waste (see “Spill, Storage, and Waste Issues” section).

**HF Spill Procedure**

If any quantity of HF is spilled outside a chemical hood or if there is a large spill (i.e., more than 10 mL) inside a fume hood, evacuate the area, close the doors, post the area with a sign to prevent others from entering, and call EHS at 413-545-2682.

Small spills of HF (i.e., less than 10 mL) inside a chemical fume hood can be cleaned up by laboratory staff if they have received spill clean-up training from EHS, it is safe to clean up the spill, they are comfortable doing so, and have at their disposal an HF spill kit.

Dispose of HF waste through hazardous waste pick up by submitting a hazardous waste request pick up through CEMS. Calcium carbonate, calcium hydroxide, calcium oxide, lime or a solid spill absorbent specified for HF should be used for neutralizing spills. Organic spill kits that contain Floor-Dri, kitty litter, or sand should not be used because HF reacts with silica to produce silicon tetrafluoride, a toxic gas.

**Emergency/First Aid Exposure Procedures**

Medical treatment is required for any hydrofluoric acid exposure. The exposed person must be treated at a hospital as quickly as possible to reduce long-term effects. Prolonged or untreated exposure can be fatal. Call 911 or the UMPD 413-545-3111 to arrange for transportation to the hospital. Always specify UMass Amherst campus and building name when calling 911.

HF is a neutral, lipid-soluble molecule, due to its small acid dissociation constant (pKₐ = 3.20), and, as such, penetrates tissue more rapidly than typical strong mineral acids which ionize readily. Because of the ability of hydrofluoric acid to penetrate tissue, poisoning can occur readily through exposure of skin or eyes, or when inhaled or swallowed. Though a weak acid, HF does liberate fluoride which can bind nearly irreversibly to calcium and magnesium, causing low levels of calcium and magnesium in the blood, and elevated levels of potassium. This can lead to:

- life threatening heart conditions
- loss of muscle function, necrosis of tissue, and bone demineralization.

Symptoms of exposure to hydrofluoric acid may not be immediately evident. This is especially true of solutions with low concentration (i.e., less than 20%) which can take several days for symptoms to develop following exposure.
HF interferes with nerve function, meaning that burns may not initially be painful. Accidental exposures can go unnoticed, delaying treatment and increasing the extent and seriousness of the injury.

**Skin Contact**

Have someone call 911. Immediately flush the affected area with cold running water for 2 minutes (use a safety shower if the affected area is larger than the size of the palm of the hand). While flushing, remove all contaminated clothing that could trap HF. Apply 2.5% calcium gluconate gel (located in the First Aid kit) with a gloved hand to the affected area. Continue irrigation with water for up to 20 minutes and reapply the calcium gluconate gel every 5 minutes. Provide the SDS to the emergency response personnel.

**Eye Contact**

Have someone call 911. Immediately flush eyes with water for at least 15 minutes with large amounts of water. Hold eyelids open and away from the eye during the irrigation to allow thorough flushing of the eyes. Do NOT use 2.5% calcium gluconate gel in the eyes. Provide the SDS to the emergency response personnel.

**Inhalation of Vapors**

Have someone call 911. Immediately move individual to fresh air. Keep the individual warm, quiet, and comfortable. If breathing has stopped, start artificial respiration, but only if a barrier or bag-valve-mask device is available. Make sure mouth and throat are free of foreign material. Oxygen should be administered as soon as possible by a medically trained individual. A nebulized solution of 2.5% calcium gluconate may be administered with oxygen by inhalation. Provide the SDS to the emergency response personnel.

**Calcium gluconate**

EH&S will provide 2.5% calcium gluconate gel to all HF user groups. The typical shelf life for calcium gluconate is one (1) year. Store calcium gluconate ointment inside the First Aid kit and notify all lab personnel of its location. Calcium gluconate gel will be tracked through the EHS CEMS system and replaced when expired. EH&S also keeps calcium gluconate on hand in case of emergencies.

**References**

Environmental Health and Safety U.T. Southwestern Medical Center: *Hydrofluoric Acid Safety.*

Occupational Health and Safety Information: Hydrofluoric Acid.  
[http://www.fap.pdx.edu/safety/hydrofluoric_acid/index.htm](http://www.fap.pdx.edu/safety/hydrofluoric_acid/index.htm)

ACGIH Guide to Occupational Exposure Values, 2013

Agency for Toxic Substances and Disease Registry, Toxic Substances Portal, CDC.  