2018

Hydrofluoric Acid Safety Guidance

Environmental Health & Safety

EHS Chemical Safety Staff

University of Iowa

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1.0 Purpose and Applicability

The purpose of this hydrofluoric acid (HF) specific chemical safety guidance is to provide basic safety information for researchers who handle HF in research labs. This safety guidance describes injury prevention, personal protective equipment (PPE), engineering controls, spill cleanup, and waste disposal. Also, this guidance provides recommendations for risk reduction via inventory reduction, prudent safety practices, and training.
This guidance is applicable to HF-handling research labs including the central microscopy facility, micro/nanofabrication facility, inorganic sample preparation labs, and other work areas where glass, metal or enamel art work may be performed by HF frosting techniques.

2.0 Introduction

HF is a unique inorganic acid. The major route of occupational exposure in research labs is skin contact with HF solution or droplets. The fluoride ions are very rapidly absorbed through the skin and eyes and cause systemic toxicity.

HF progressively releases fluoride ions and the 'free fluoride ions' penetrate and spread into the deepest tissues, resulting in liquefactive necrosis (also known as colliquative necrosis, tissue death that liquefies the affected cells), hypocalcaemia (low calcium levels), hypomagnesaemia (low magnesium levels), and hyperkalemia (high potassium levels). ***The liquefactive necrosis mechanism differentiates HF from other strong acids which cause damage via the 'free hydrogen ions', thus causing coagulation necrosis with precipitation of the tissue proteins.*** Guidelines for the management of cutaneous, inhalation, ingestion, and ophthalmic burns from HF exposures are described by Hatzifotis, et al (2004). Injury and illness prevention is the most significant part of HF management in research labs because internal damage can occur before symptoms appear.

3.0 Injury and Illness Prevention

First Aid Kit

The location of an HF-specific first aid kit must be known to everyone in the lab and must be within quick reach of the designated fume hood or HF work area.
The contents of the HF first aid kit should be verified prior to the start of HF work each day.

- The injury and illness prevention measures for HF-handling labs require stocking of calcium gluconate gel (CG gel) in the HF-specific first aid kit. Calcium gluconate eyewash solution (CG solution), and a container of antacid tablets (for example, regular strength antacid 0.5 g $CaCO^3$ per tablet, 150 tablets) are also recommended.
- Typically, an expiration date is noted on CG tube and the packaging.
- Whenever possible, CG concentrate or gel should be stored in a refrigerator.
- Prior to handling HF in the laboratory, researchers should ensure the availability of an unopened tube of CG gel (skin protection), CG solution (emergency eye wash) and that they have not passed their useful shelf life.

- Calcium carbonate antacid tablets are to be used as first aid to treat accidental ingestion as a first aid.

- On an as-needed basis, calcium gluconate slurry or gel can be prepared in-house by adding 2.5 g calcium gluconate in 100 ml of water soluble lubricant, such as K-Y Jelly.
- When needed, crushed calcium carbonate tablets can also be used to treat a small incidental spill, typically less than 2 ml.

Emergency/Medical Treatment

- First aid measures MUST BE started within seconds in the event of HF contact in any form or concentration!
- If HF is not rinsed off immediately after the exposure, severe burns and skin damage will definitely occur.
- Even at very low concentrations, HF can be irritating to the respiratory tract, eyes, and skin.

Without delay, rinse the affected skin area with water at least for 20 minutes and apply CG gel to bind the fluoride ions which prevents further tissue destruction. Even if the affected employee feels no pain, the affected area must be immediately rinsed off with copious amount of cold water at least for 20 minutes, followed by application of CG gel to the affected skin area. Researchers must then seek immediate medical attention for HF burns BY GOING TO THE UIHC EMERGENCY TREATMENT CENTER (ETC).
If the spill has occurred near the eye, eyelid, or eyelash, irrigate exposed or irritated eyes with cold water **for at least 20 minutes**. The 20 minutes **may be** limited to 5 minutes **only if** a CG eye wash solution is readily available and is used immediately after the 5 minutes of cold water rinse, and the individual proceeds to ETC without delay.

Ingestion of HF can cause severe mouth, throat and stomach burns. In case of ingestion, dilute the acid by giving large quantities of water and eight to twelve Tums®, Rolaids® or Walgreen antacid tablets, and proceed to ETC without delay. DO NOT induce vomiting.

If no one is immediately available to assist you or drive you to ETC, call 911 and let them know you have a medical emergency with HF exposure such as splatter near the eyelid or other parts of the body.

A medical evaluation is necessary for any exposure to HF. Additional medical treatment/consultation should follow with appropriate medical specialists for eyes and/or skin burns. For detailed medical treatment, please review the Honeywell reference document, “Recommended Medical Treatment for HF Exposure.”

4.0 Safety Equipment

A properly functioning eyewash station and a safety shower should be available in the immediate work area.

5.0 Engineering Controls

Any work involving HF or other HF-containing reagents should be performed inside a properly functioning chemical fume hood. Fume hoods made with polyethylene (PE), polypropylene (PP), or PVC/PP and polycarbonate sashes are appropriate for HF work. These fume hoods often have ducts that are coated with PTFE (Teflon) liners.

6.0 Personal Protective Equipment (PPE)

- Principal investigators and lab managers should ensure proper PPE is available for their staff and students.
- When working with HF, safety glasses with side shields are not adequate.
- When handling large quantities of HF or working with HF baths, thick Nitrile (14 mil or thicker) or full length rubber sleeves, butyl rubber apron, face shield, and chemical splash goggles should be worn.

The recommended PPE for working with HF includes face shield and chemical splash goggles to protect against chemical splash, acid resistant Neoprene or Viton outer gloves and inner double Nitrile gloves, full sleeve lab coat, chemical resistant apron, and long pants.

- At a minimum, double Nitrile gloves (4 mil thick) or butyl rubber gloves are strongly recommended when working with small quantities of HF.
- Silver shield gloves with inner double Nitrile gloves can be used for spill cleanup work.
- If dexterity of silver shield gloves impacts the handling of HF, review chemical resistance charts for other glove options.
  - Neoprene gloves have good dexterity. Ansell Brand Dermashield gloves are rated to have good dexterity and suitable for clean room operations.
- Butyl rubber aprons suitable for HF work should be used for HF work with concentrations at or above 1 M acid strength (i.e., ca. at or above 2% HF), or processes having a splash/splatter potential. Rubber aprons may be purchased from Fisher Scientific or Grainger.

7.0 Prudent Work Practices

WHEN WORKING WITH HF IN THE LAB, DO NOT WORK ALONE.

- Due to the unique physiochemical properties of HF, additional precautions are required, as compared to other inorganic acids.
- Researchers must thoroughly wash their hands after handling HF bottles and reaction vessels.
- Hands-on training should be provided to all researchers working with HF under the direct supervision of the PI or Lab Manager.

The work area must be designated for HF use. Signage (warning notice) must be posted at the fume hood or door to the room when HF is used.

Depiction of Example Signage

- HF specific signage is not required on a storage cabinet when it is kept within a corrosive storage cabinet (e.g., an acid cabinet under the fume hood).
- If HF is used on a daily basis or used frequently every week, the HF bottle can be stored within a fume hood with a warning sign indicating “HF is stored in this hood.”
- A standard operating procedure (SOP) should be implemented for HF work. The SOP should include process description (e.g., heated HF process, silicon wafer or glass surface cleaning and etching, sample digestion, HF use quantities, concentration, and temperature, etc.), PPE (manufacturer, model and type), process specific safety precautions, container labeling, emergency/medical treatment, spill cleanup, and waste disposal. A site specific HF procedure should include the location of the eyewash and shower.
- At a minimum, a rubber bottle carrier should be used for transporting HF bottles between the storage cabinet and fume hood. A fully enclosed secondary container is recommended to protect the primary container during storage and transport.

Rubber Bottle Carrier and Enclosed secondary container

For high risk HF operations, a daily preoperational checklist including first aid kit, PPE, and spill cleanup supplies may be implemented by the PI.

- Only use labware made of PE, PP or PTFE.
- A buddy system such as a two-person rule is encouraged for high risk operations (see Appendix B). A buddy system allows less experienced researchers and undergraduate students to learn more quickly from close and frequent contact with an experienced researcher in the lab.

8.0 Hazard Evaluation and Process Risk Reduction Assessment

Danger:

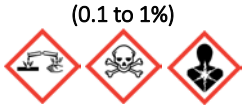
- **HF is highly corrosive to metals, glass, skin, tissues and bones.**
- **Any HF work must be performed within a chemical fume hood**.

Hazards Evaluation

HF is one of the most corrosive inorganic acids. Per GHS classification of chemicals, HF is both a physical hazard (corrosive to metal, glass, enamel, etc.) and a health hazard (acute poison and corrosive to skin, eyes, respiratory system, bones, etc.) as shown in the pictograms below.

- HF is acutely toxic and extremely destructive to the body tissue and respiratory tract.
- Exposures to HF will result in skin burns. Dermal exposure will cause severe and painful burns.
- HF in any concentration and quantity is highly hazardous to the human body system.

Below are example pictograms, hazard statements, signal words, and risk statements for different HF concentrations in water or other formulations.

GHS Pictograms	Hazards and Signal Word	Risk Statements
HF conc. ≥ 3 M (≥ 6%) 	**Danger - Corrosive to respiratory and body** systems, eyes, and bones. Ingesting~1.5 ml of 40% HF is fatal.	Acutely toxic if inhaled, in contact with skin, and if swallowed. Causes severe burns.
	**Warning - Corrosive to metals** (Conc. HF is typically used for stripping industrial parts made of stainless steel.	
HF conc. 0.5 M to <3 M (1 to <6%) 	**Danger - Corrosive to respiratory and body systems, eyes, and bones.**	Toxic if inhaled, in contact with skin, and if swallowed. Causes burns.
	**Warning – Corrosive to metals**	Corrosive to metals
HF conc. 0.05 M to 0.5 M (0.1 to 1%) 	**Danger - Corrosive to respiratory and body systems, eyes, and bones.**	Harmful if inhaled, in contact with skin, and if swallowed. Irritant for the eye, the respiratory track and the skin.

Risk Reduction Assessment

Whenever possible, researchers should consider elimination or substitution of HF with less dangerous reagents, changing procedures to minimize the amount of HF used, or alternate processes. A basic risk assessment for various activities including risk minimization recommendations for safe handling of HF is summarized below.

HF Storage or Process Application	Recommendations for Risk Reduction	Typical Storage, Usage Quantity and Frequency of Use	Storage or Process Risks
Storage (concentrated acid)	o When not in use, tightly seal the container. o Store HF reagent bottles in a secondary storage container within a corrosive acid cabinet. o Label the secondary storage container (an example of labeled secondary containers is depicted in section 7). o **Minimize HF inventory to one or two bottles.**	More than two 500 ml HF bottles (40% or higher concentration)	**High**
		Two 500 ml HF bottles (40% or higher concentration)	**Moderate**
		One 500 ml HF bottle (40% or higher concentration)	**Low**
Storage (diluted solutions)	o Store HF reagents tightly capped in PE or PP containers. o Store diluted HF solutions (≥3 M) in a labeled secondary storage container within a corrosive acid cabinet or in a polyethylene tray within a fume hood. o Label all in-house prepared reagent containers and samples containing HF.	Diluted HF solutions and synthetic reagents	**Low**
Aliquoting, pouring or dispensing HF to reaction vessels	o Develop and implement written SOPs. o Work within a fume hood. o Develop and implement written SOPs. o Wear a face shield, chemical splash goggles, appropriate gloves, and lab coat. Wear apron over lab coat.	Pouring or dispensing to reaction vessels per event, twice monthly. (Typically 2 to 20 ml per reaction vessel, 10 samples per event.)	**High**
Digestion of geologic rocks or clay minerals	o Develop and implement written SOPs. o Work within a fume hood. o **WHERE APPROPRIATE, SASH MUST BE KEPT CLOSED ALL THE WAY DOWN**	2 to 20 ml per sample and no more than 10 samples per event, twice monthly. (Digestion is performed with sash closed and therefore	**Moderate**

	o Wear a face shield, appropriate gloves, and lab coat. o Wear apron over lab coat if splash potential exists. o Ensure fume hood face velocity is within the working range to prevent any fugitive SiF_4 emission in to the lab environment from digestion process.	risk is lower than the dynamic pouring/ dispensation activity.)	
		< 2 ml per sample and no more than 5 samples, twice monthly.	**Low**
Cleaning/etching of silicon wafer, metal, or glass surface	o Develop and implement written SOPs Work within a fume hood. o Wear a face shield, chemical splash goggles, appropriate gloves, and lab coat. Wear apron over lab coat. o When not in use, sash must be closed all the way down.	2 - 10 ml per sample and no more than 10 samples, twice monthly.	**High**
		< 2 ml per sample, no more than 5 samples, twice monthly.	**Moderate**
Pyridinium hydrofluoride (synthetic reagent)	o Develop and implement written SOPs. o Work within a fume hood. o Wear a face shield, appropriate gloves and lab coat. o When not in use, tightly seal the container and store in a dry, cool place.	< 5 ml per sample per event.	**Moderate**
Dilute trifluoroacetic acid (TFA) in water	o **Warning:** TFA can hydrolyze to HF upon contact with moisture. o Wear chemical splash goggles, appropriate gloves and lab coat. o TFA mobile phase should be prepared within a fume hood.	Typically used as 0.1% TFA in water as HPLC mobile phase.	**Moderate**
Spill cleanup (HF spill outside of a fume hood)	o ***Danger: HF vapors are harmful to respiratory system (OSHA PEL is 3 ppm).* All HF work should be performed within a fume hood.** o ***For any quantity or any concentration less than 250 ml:*** o *Alert everyone in the lab to evacuate until cleanup is finished.* o *Call EHS Emergency Response Coordinator with questions if needed (5-8501, business hours).* o Wear a face shield, chemical splash goggles, appropriate gloves, and lab coat. Wear apron over lab coat.	Any quantity and any concentration outside of the fume hood.	**Moderate to High**

	o *Contain the spill and cleanup using supplies in the spill kit designated for HF.* o ***For any quantity or any concentration greater than 250 ml:*** o *Call 911. Inform dispatcher that an HF spill occurred outside of the fume hood. Wait for instructions from response team.* o *Alert everyone in the lab to evacuate until cleanup is finished.* o *During business hours, contact the EHS Emergency Response Coordinator <u>to explain details of the spill</u> (5-8501).*		
Spill cleanup (within a fume hood)	o Wear a face shield, chemical splash goggles, appropriate gloves, and lab coat. Wear apron over lab coat.	>500 ml	**High**
		20 to 500 ml (Both concentrated and dilute HF)	**Moderate**
		5 to 20 ml (Both concentrated and dilute HF)	**Moderate**
		<5 ml (Both concentrated and dilute HF)	**Low**
Waste Disposal: Transport of either unused HF or diluted HF soln.	o Concentrated HF stored in original containers will be picked-up for disposal by EHS. o Diluted HF reagent and lab generated HF waste <u>must be</u> properly neutralized and stored in PE or PP containers for disposal by EHS. o **HF-waste, including neutralized HF-waste, should not be stored in glass bottles.** o See PPE section for appropriate PPE.	<u>Concentrated HF soln.:</u> 40% or higher in original container. <u>Diluted Soln.:</u> Process specific diluted HF reagents, process wastes, etc. should be stored in PE or PP container.	**Low**

9.0 Spill Cleanup

- **HF is a unique inorganic acid and does not completely dissociate. Therefore, researchers should allow sufficient time for the neutralizing agents to neutralize the acid.**
- **Properly dispose of waste from HF cleanup work using polyethylene containers.**
- **HF spillage should be contained and avoid allowing the spill to go down the drainage sink in the fume hood, if possible. If necessary, neutralized liquid within the fume hood should be diluted with copious amount of running water.**
- **For detailed spill response, please review** EHS spill response guidelines **.**

A spill containing HF should be neutralized with calcium hydroxide, calcium carbonate, or other magnesium salts.

- Spill kits containing silica such as sand, vermiculite, Floor-Dri or kitty litter should not be used because HF reacts with silica to produce a toxic silicon tetrafluoride (SiF_4) gas.
- Commercially available HF specific spill kits include spill absorbent materials such as 3M universal adsorbent, HF Acid-Eater (NPS Corp) or HF Spill Tamer (JT Baker/Mallinckrodt), Kolor-Safe® Kolor-Lock powder, and PIG® HF neutralizer. Silver shield gloves with inner double Nitrile gloves can be used for spill cleanup work.

Depiction of Commercially Available Spill Kit

- The HF spill kit should also include thick chemical resistant gloves (2 pairs, 14 mil or higher thickness), chemical splash goggles (at least 1), polyethylene bags (2 bags, 4 mil thickness). Commercially available spill kits may also include: HF spill adsorbent/neutralizer materials, 2 aprons, 2 pairs of gloves, hazmat boot covers, 2 pairs of goggles, MSDS and cleanup instructions.
- Calcium based neutralizers convert HF to an insoluble calcium fluoride salt.
- Small amounts of HF spill in the fume hood (<2 ml, 40% or less) can be absorbed using calcium carbonate antacid tablets (15 tablets, 500 mg each). Dilute the spilled area with water and then neutralize the acid cautiously using crushed tablets.

- **HF with concentrations greater than 40% will generate fumes in air.** Therefore, the spilled area must be carefully and rapidly diluted to less than 40% concentration with water and then neutralized using calcium hydroxide slurry or other commercial spill materials. The effectiveness of the neutralization should be checked with pH paper.
- HF cleanup waste should be collected separately and EHS should be contacted for disposal.
- Researchers using boric acid for HF spill cleanup and neutralization should collect the resulting solution for disposal by EHS.
- **Any HF spill greater than 250 ml outside of a fume hood should be treated as a large spill.**
- Call 911 for any large spills (if the spill is greater than 250 ml HF outside of a fume hood).
- See risk reduction assessment table for additional detail.

10.0 Waste Disposal

- Do not mix HF with other laboratory generated waste.
- Use polyethylene bottles and polyethylene caps for collecting solution containing HF.
- Label waste containers with hazardous waste labels.
- Dispose of HF through EHS by completing an online hazardous waste pickup form.

When labeling the waste bottles, researchers must not abbreviate hydrofluoric acid as HF. HF is highly reactive with silica and will attack glass bottles with the formation of toxic SiF_4. Therefore, HF waste must be collected in a chemically compatible container. Non-reactive HF compatible containers include PE, PP or PTFE bottles.

- HF waste should not be mixed with any other laboratory waste.
- Researchers using boric acid to neutralize HF as water soluble fluoroboric acid should collect the resulting solution for disposal by EHS.
- A waste pickup request must be submitted to EHS. Use the EHS online hazardous waste pickup form for the disposal of HF waste.

11.0 References

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Acknowledgements

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Appendix A

Hydrogen Fluoride Permeation Data for Various Gloves Materials

Material Breakthrough time (in hours)	
Butyl Rubber	>4
Natural Rubber	1 to 4
Neoprene	1 to 4
Polyethylene	1 to 4
Nitrile Rubber	<1(*)
Polyvinyl Alcohol	<1(*)
Polyvinyl Chloride	<1(*)
(*) not recommended, degradation may occur	

Appendix B

This example HF training documentation can be pasted on to researcher's lab notebook page. Alternatively, HF training records can be collocated with PPE-HAT documentation. Buddy system training allows less experienced researchers and undergraduate students to learn more quickly from close and frequent contact with the experienced researcher within a lab. During the hands-on HF training, both trainer and trainee should be able to communicate verbally and be within hearing distance of each other.

Department: _____ Date of Training: _____

PI Name and Signature: _____ _____

Trainer Name and Signature_____ _____

Trainee Name and Signature: _____ _____

By the signatures of the PI, trainer and trainee listed above, we certify that the trainee has demonstrated his/her understanding of safe HF handling practices in our research lab.

_____ Trainee has reviewed the HF specific chemical safety located in EHS website (this guidance document).

_____ Trainee has reviewed the process specific standard operating procedure (SOP).

_____ Trainer discussed the injury and illness prevention measures including first aid supplies and emergency/treatment.

_____ Trainee was shown the location of HF specific first aid kit including CG gel and CG eyewash solution, and spill response supplies.

_____ Trainee was shown HF specific waste collection and storage method(s).

_____ Trainee was provided appropriate process specific lab coat, apron, face shield and chemical splash goggle to protect against chemical splash/splatter.

_____ Trainee was shown HF storage location and safe transport of HF in a rubber bottle carrier.

_____ Trainee satisfactorily transported HF bottle from storage cabinet to fume hood and then returned to storage.

_____ Trainee satisfactorily demonstrated the dispensation and process handling techniques, and waste collection and storage in a polyethylene/polypropylene container.

_____ Trainee satisfactorily demonstrated the correct fume hood sash height and able to recognize acceptable face velocity range in FPM if a Magnehelic gauge or digital velometer is installed.