Standard Operating Procedure
for work with

Chemical name/class:	**Hydrofluoric Acid (HF)**	**CAS #:**	**7664-39-3**
PI:	**Mark Walters**	**Date:**	**March 1, 2021**
Building:	**Fitzpatrick CIEMAS**	**Room #:**	**Cleanroom and Sample Prep**
		Designated Work:	**Chemical processing with Hydrofluoric Acid**

1. **Circumstances of Use:**

Hydrofluoric Acid (HF) is typically used in SMIF for etching oxide films. It is used in the lab directly out of the bottle (49% concentration), diluted with water, and as the active component of BOE, Buffered Oxide Etch.

2. **Potential Hazards:**

Consult the Safety Data Sheet (SDS) for Hydrofluoric Acid.

Hydrofluoric acid, HF, presents a significant hazard for personal injury. It is a high risk category 1 chemical because it can be fatal in contact with skin.

Be aware of these specific hazards:

- Liquid HF is one of the strongest and most corrosive acids. It can be irritating to the skin, eyes, and respiratory tract. Contact with exposed body parts can cause painful burns and even death.
- In high concentrations (more than 50%), HF usually causes immediate burns that are extremely painful and slow to heal.
- In lower concentrations, exposure may not be apparent for several hours, but can still cause burns and further damage if not washed off.
- HF causes such severe burns because it penetrates beneath the skin and dissociates into hydrogen and fluoride ions. When fluoride ions bind with calcium in the body, it can result in tissue destruction, decalcification of bone, cardiac arrhythmia, and liver and kidney damage.
- The OSHA Permissible Exposure Limit for hydrogen fluoride is 3 ppm. The American Conference of Governmental Industrial Hygienists recommends a ceiling (instantaneous) limit of 2 ppm and an 8-hour limit of 0.5 ppm.

3. **Engineering Controls:**

- Always work with HF in a designated acid fume hood in the Clean Room or Sample Preparation Lab.
- An eyewash and safety shower are available in the immediate area.

4. **Work Practice Controls:**

- Use only in a designated acid chemical hood.
- Keep containers closed as much as possible. Only open a container when it is inside a designated acid chemical hood and you are wearing the proper PPE (section 5).
- When diluting, add HF to water slowly, in small amounts. (Never add water to HF)
- Contaminated items are to be disposed of properly as hazardous waste, following SMIF's hazardous waste policy (see section 7).

5. **Personal protective equipment (PPE):**

- Wear chemical gloves
  - Always first check chemical gloves for holes or damage
    - If damaged, dispose of the gloves and get a new pair
  - Never purposefully touch a chemical even while wearing the chemical gloves. If a glove does come in contact with a chemical
    - Remove the exposed glove and dispose of it.
    - Get a new pair of gloves
  - Wear gloves to open chemical cabinets.
  - Wash and remove gloves before touching anything else (door knobs, notebooks, phone, microscopes, etc.)
- Wear chemical splash goggles (safety glasses are not sufficient).
- Wear a face shield.
- Wear a chemical-protective gown with sleeves.

6. **Transportation and Storage:**

- Hydrofluoric Acid must be in sealed shatter-resistant containers and stored in an exhausted chemical cabinet designated for acids.
- Wear the designated PPE (section 5) when transporting an HF bottle or container to a chemical hood.

7. **Waste Disposal:**

Liquid Waste

Pour all HF waste into the acid hood sink drain for proper disposal. These drains lead into a house acid waste neutralization system.

- Press the **Drain** button to open the drain
  - The drain will not open if chemicals are above 50ºC
  - The drain has a water dilution in it to reduce the chemical waste concentration
- Rinse the sink with water from the gooseneck or water sprayer after draining chemicals to wash out any residues
- Press the **Drain** button to close the drain. ***Do not leave the drain open if it is not needed.***

Solid Waste

Solid materials that are contaminated with chemical HF waste (such as wipes, dispensers, etc.) should be packed into a zip lock bag and properly labeled with the type of waste, your name, and date. The waste bag should be completely sealed.

- Bagged and labeled solid HF waste can be left in the back of the hood for pickup by SMIF staff
- Empty HF bottles should be rinsed in the sink and left in the hood for pickup by SMIF staff

8. **Exposures/Unintended contact:**

Contact Employee Occupational Health and Wellness (EOHW) at 919-684-3136 for medical advice on occupational chemical exposures. For an actual HF chemical exposure:

Simple washing of an HF splash is not sufficient to prevent damage. If you suspect you have been exposed to HF, you should immediately do the following:

1. Rinse off the exposed area with water (e.g., the safety shower) for 5 minutes
2. Immediately apply Calcium Gluconate Gel to the exposed area. This Gel can be found at all Acid Hoods in SMIF.
3. Call 911 from a campus phone or 919-684-2444 from any phone and request immediate medical assistance. Be sure that medical personnel know that it is an HF burn and know that it requires specific treatment different from a common acid burn**. Make sure that a copy of the HF Medical Treatment and First Aid Guidelines are available to medical personnel.**

Complete First Aid Guidelines for Treating HF exposures can be found as an Appendix to this manual, and printed copies are available at all SMIF Acid Hoods and the SMIF Emergency Response Station.

Contact Employee Occupational Health and Wellness at 919-684-8115 for exposure-related advice.
The work-related injury or illness report found at: http://www.hr.duke.edu/benefits/medical/workcomp/report.php should be completed within 24 hours. Follow-up medical attention should be sought through Duke Employee Occupational Health and Wellness (919-684-3136).

9. **Spill Procedure:**

In the event of a spill, follow SMIF spill procedures and immediately contact SMIF staff. Only SMIF staff and/or appropriate OESO personnel should clean up spills

Spills Contained Inside a Chemical Hood

- Avoid breathing vapors from the spill and leave the immediate area of the chemical hood
- Alert people in the immediate area of the spill
- Notify SMIF immediately by calling emergency numbers posted near the phone
- Wait for instructions from SMIF or for SMIF personnel to arrive to complete the clean-up of the affected area.

Spills Outside of a Chemical Hood

- Attend to injured or contaminated persons and remove them from exposure
- Press the closest manual alarm button (blue box) and evacuate the lab
- Make yourself available to the SMIF staff and/or emergency responders and be prepared to tell the following: What chemical(s) are involved, how much was spilled, where the spill is located, nature of any injuries

10. **Training of personnel:**

- All personnel are required to complete the SMIF General Lab Safety session and the SMIF Chemical Safety and Wet Hood training session.
- All personnel shall read and fully adhere to the ***Wet Hood Operating Procedure*** and the ***SMIF Lab Safety and Procedures Manual***

DANGER!

Duke OESO Guidelines for Safe Use of

Hydrofluoric Acid

Lab-specific Safety Information on page 3 MUST BE APPROVED in advance by OESO and the PI.

DANGER!

Hazards

Potential Hazards

- **Fatal if swallowed, in contact with skin, or if inhaled.**
- Causes **severe skin burns** and **eye damage**.
- See also the SDS for your product & the Lab Chemical Safety Summary for hydrofluoric acid.
- Exposure limits: ACGIH TLV – 2 ppm ceiling, 0.5 ppm average over 8 hrs. OSHA PEL: 3 ppm.
- *Hydrofluoric acid penetrates the skin and dissociates into hydrogen and fluoride ions, which can subsequently cause tissue destruction, decalcification of bone, cardiac arrhythmia, and liver and kidney damage. >50% hydrofluoric acid usually causes immediate burns that are extremely painful and slow to heal. Exposure to lower concentrations may not be apparent for several hours but can still cause burns and further damage if not washed off.*

Hazard Controls - 1

Selection & Purchase

- Consider the use of an **alternative acid**.
- Purchase the **smallest container** at the **lowest concentration** practical.
- Stock **benzalkonium chloride** solution (0.13%) or **calcium gluconate gel** (calgonate.com)

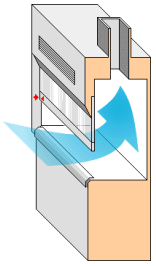
Storage & Transport

- Store in compatible (e.g. polyethylene) **primary** and **secondary** containers.
- **DO NOT** use glass containers – hydrofluoric acid dissolves glass. **No Glass!**
- Keep the primary container tightly closed.
- Store in a **dry** and **well-ventilated** place.
- Store **below eye level** but **not on the floor**.
- **Store away from bases, metals, and other incompatible materials**.
- **DO NOT** store under the sink.
- Transport in a **bottle carrier**.

Engineering Controls & Safety Equipment

- **Eyewash and drench hose** are required in the immediate work area.
- A **safety shower** will also be necessary for most uses of hydrofluoric acid. Contact OESO at 684-8822 about the need for a shower if there is not one available.

- All work must be done in a chemical fume hood.



Work Practice Controls

- *Use page 3 to create a lab-specific SOP and get PI approval signature.*
- Before using, make sure benzalkonium chloride or calcium gluconate gel are not expired.
- Have an **area** in the laboratory that is exclusively **designated for hydrofluoric acid use**.
- **Post warning signs** in both the designated area and on the door to the room when in use.
- Work within sight and/or hearing of **at least one other person** who is familiar with the hazards and lab-specific written procedures.
- **Line all work surfaces** with plastic-backed absorbent paper and/or a containment tray that is compatible with hydrofluoric acid.
- Always **add** hydrofluoric **acid to water** and not the reverse.
- DO NOT use glass, ceramic or other incompatible containers.
- DO NOT heat.
- DO NOT breathe hydrofluoric acid vapors, mists, or gas.
- DO NOT get in eyes, on the skin, or on clothing.
- **Wash hands** immediately after handling.
- Once work is complete, **decontaminate** the area by wiping with a 10% sodium carbonate (Na_2CO_3, also known as soda ash) solution.

Hazard Controls - 2	**Personal Protective Equipment**	**Eyes & Face**: Tight fitting safety **goggles** and **face shield** (8" in length, minimum) **Hands:** Use 5 mil **Neoprene** for <50 ml of 48% or less. *Change gloves every 30 min.* For >50 ml, >48%, or for spills: use 17 mil (or thicker) Neoprene, 14 mil (or thicker) butyl, or 5 mil neoprene over laminate (e.g., Silver Shield). • *Inspect gloves for defects prior to use.* • *Remove gloves after handling and take care to not touch the outer surface of the glove.* **Body:** Fully buttoned lab coat, sleeves to the wrist; Clothing covering legs; Closed toed shoes; Rubber apron; Chemical-resistant sleeves.       
Other	**Medical Emergencies**	***Immediate first aid and medical treatment*** *are essential for people exposed to hydrofluoric acid.* People working in and around hydrofluoric acid should be familiar with the Hydrofluoric Acid First Aid Guidelines. These guidelines should be printed and kept with first aid supplies. **For an actual chemical exposure/injury:** • Seek **immediate medical attention** at the **emergency department** for any exposure. Show SDS and Hydrofluoric Acid First Aid Guidelines to the medical provider(s). • *Persons helping an exposed colleague must wear PPE as indicated above.* • Call 911 from a campus phone or 919-684-2444 from any phone to request immediate help. • Contact Employee Occupational Health and Wellness (919-684-8115) for exposure-related advice. Complete the Injury/Illness report after seeking treatment. • Benzalkonium chloride (such as Zephiran) or calcium gluconate gel will bind to the fluoride ions and prevent further tissue destruction, but to be effective they must be applied quickly, even before burns are felt. **Skin exposure:** • Flush with water for 5 minutes then soak area in an iced (cubes not shaved) benzalkonium chloride (0.13%) solution or rub calcium gluconate gel onto the burn site. Continue to soak in benzalkonium chloride or massage the calcium gluconate gel into the burn site during transportation to a medical facility and while waiting to see a physician. • If immersion in benzalkonium chloride solution is not practical, soaked compresses of the same iced solution should be applied to the burned area. • If not using calcium gluconate gel, continually rinse with water until treatment is provided. **Eye exposure:** • Flush eyes for at least 15 minutes with large amounts of gently flowing water. • If sterile calcium gluconate solution (1%) is available, flushing eyes may be limited to 5 minutes. Afterward, use a syringe (no needles!) to repeatedly irrigate the eye(s) with the 1% solution. • Take the victim to a doctor, preferably an eye specialist, as soon as possible. Use ice water compresses on the eyes during transportation. **Inhalation:** Remove victim to uncontaminated area. Seek immediate medical attention. **Ingestion:** DO NOT INDUCE VOMITING. Seek immediate medical attention.
	Spills	• **Spill >5 ml:** On Duke's Durham campus, any spill >5 ml hydrofluoric acid must be referred to the OESO spill team by calling 911 from a campus phone or 919-684-2444 from any phone. • **Spills <5 ml:** Absorb using magnesium sulfate, soda lime, sodium carbonate (Na_2CO_3), or other spill absorbent specified for hydrofluoric acid. **DO NOT** use organic spill kits containing Floor-Dri, kitty litter, or sand because a toxic gas (silicon tetrafluoride) will be created. • **AFTER** the spill has been absorbed, use a 10% sodium carbonate solution to clean the area. • See Emergency Response webpage or flip chart and/or lab specific chemical hygiene plan.
	Waste	See lab-specific chemical hygiene plan or Lab Chemical Waste Management Practice.
	Training	Sign lab-specific SOP to indicate review.
	Questions	Contact OESO Lab Safety 919-684-8822.

Lab-Specific Safety Information for

Hydrofluoric Acid

Supplements the Guidelines for Safe Use of Hydrofluoric Acid

Must be approved by OESO and PI below.

Lab	**PI Name**	Mark Walters	PI Approval (signature): Date: 3/1/2021	
	Location	Fitzpatrick CIEMAS – SMIF Cleanroom and Sample Prep Lab		
	OESO Approval	Click or tap here to enter OESO Reviewer	Signature: Date: Click or tap to enter a date.	
Lab-Specific Hazard Controls	**Purchase Details**	Maximum container size	Enter maximum container size purchased	
		Maximum concentration	Enter maximum concentration purchased	
		Container type	Enter the container material	
		Specific product info.	Enter supplier name/product number or purity/grade to purchase	
	Storage	Specific location	**Acid Chemical Cabinet**	
	Use Information	Designated work area (specific room(s) and area(s))	Acid Wet Hoods	**Label work area!**
		Type of container to use	Type of container in which HF is used or stored in the lab	**NO GLASS!**
		Maximum quantity	Enter maximum quantity to be used at a time	
		Gloves (Note other PPE requirements in Guidelines)	**Necessary glove for handling <50 ml:** ☐5 mil neoprene gloves (change every 30 minutes) **Necessary gloves for handling >50 ml or for cleaning spills < 5 ml:** ☐17 mil (or thicker) neoprene gloves ☐14 mil (or thicker) butyl gloves ☐5 mil neoprene gloves over laminate (e.g., Silver Shield) **PPE Location:** Indicate where special PPE for hydrofluoric acid is stored	
		Location of Na_2CO_3	Indicate where sodium carbonate (for decon) is stored	
	Emergency Information	Type of spill absorbent	☐ Magnesium sulfate ☐ Soda Lime ($CaHNaO_2$) ☐ Sodium Carbonate (Na_2CO_3) ☐ Other sorbent specified for hydrofluoric acid (NOT an organic material such as Floor-Dri or kitty litter, and NOT sand): Indicate another type of HF-compatible sorbent to be used	
		Location of spill supplies	Indicate where spill supplies are stored	
		Location & Type of First Aid Materials	Indicate where first aid supplies are stored	☐ Benzalkonium Chloride (0.13%) ☐ Ice cubes (not crushed or shaved) OR ☐ Calcium gluconate gel

	Waste Information	Details about waste – location, type of container	Indicate location & type of container used for waste accumulation	**NO GLASS!**
	Details of Process	1. Enter steps used in lab process(es) or experiment(s)		