

# Hydrofluoric Acid (HF)

## Standard Operating Procedure

Lab: Beckman Institute 3724

Department: Materials Science and Engineering

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### Section 1: Overview

Type of SOP:  Process  Hazardous Material  Hazardous Class of Materials  Equipment

#### Synopsis:

The purpose of this SOP is to ensure that the users of the Braun Group laboratories are aware of the hazards and proper handling of Hydrofluoric Acid (HF) and to ensure that the users of the HF hood in Beckman Laboratory Room 3724 know the silicon etching procedure.



## Section 2: Risk Assessment Summary (Hazards and Control Measures)

### Materials:

Material (name, CAS #, other ID)	Hazards
Hydrofluoric acid, 7664-39-3	Target organ effect Toxic or fatal by skin absorption Toxic or fatal by inhalation Toxic or fatal by ingestion Extreme damage to eyes upon contact Causes skin and eye burns Corrosive Explosive hydrogen gas released when reacting with certain metals

### Relevant References for Material Hazards:

- [MSDS](#)
- [Other References](#)

### Hazardous Conditions:

- **Appearance and Odor** HF is an extremely toxic and colorless liquid. HF has an irritating odor, but fume levels can reach dangerous levels with no obvious odor. Fumes will be formed by HF concentrations above 40%.
- **Reactivity** HF is extremely reactive. Contact with metals such as iron or steel releases flammable hydrogen gas. HF also reacts with glass, concrete, water, oxidizers, reducers, alkalis, combustibles, organics, and ceramics, and should be kept away from all of these types of materials. In Braun laboratory, HF should only be stored or transported in polypropylene.
- **Health Effects** Contact with HF can be fatal. HF can be absorbed through the skin, and once in the blood stream HF reacts with blood calcium leading to cardiac arrest. Contact with HF also causes burns and tissue damage and interferes with nervous function. If HF makes eye contact it can cause blindness. If HF is inhaled it can cause fluid accumulation in the blood, irregular heartbeat, difficulty breathing, coughing, and irritation, and large air spaces in the lungs. Long term exposure can cause weakened bone structure, skin disorders, and respiratory, liver, and kidney issues. If exposed to low concentrations of HF, symptoms may be delayed for many hours or a few days, making HF extremely dangerous.
- **HF is Incompatible With** Glass, metals, strong bases, alkalis, silica, cyanides, carbonates, reducers, and ceramics are all incompatible with HF. In Beckman Institute, we use polypropylene containers and (high-density) polyethylene pipettes.

### Equipment Hazards:

- A magnetic stirrer is used, which doubles as a hotplate. Never turn the hot plate on when using HF. HF itself is not flammable, but if a fire occurs highly corrosive and toxic hydrogen fluoride gas may be released. Additionally, HF can release flammable hydrogen gas when in contact with metals.
- When using a high-density polyethylene or polyethylene pipette, never tilt the pipette back, or HF droplets may travel to the end of the pipette and damage it, potentially resulting in a spill.

- Sometimes residual HF can be stuck in the pipettes from previous uses. Ensure that a pipette is empty before using it to prevent spills and splashing.
- Syringes are sometimes used to score porous silicon. Be careful not to injure yourself when using syringes.

#### Technique Hazards:

- HF spills and splashes can occur when transferring HF to and from its container.
- Tape is required to hold down the sample. If tape is applied incorrectly it may result in a spill. Only apply tape to the very most corners of the samples, avoid applying tape towards the center of the sample.

#### Personal Protective Equipment

- HF users should wear safety glasses, three pairs of Nitrile gloves, latex-free HF approved gloves that cover forearms if desired, a lab jacket, a butyl rubber apron, a face shield, long pants, and closed-toe shoes should be worn.
- All HF processing should be done at least 6 inches inside an operational and inspected fume hood.

#### **Gloves tested by manufacturer for hydrofluoric acid solutions 48% (From: UIUC DRS)**

Manufacturer	Glove	Material	Thickness	Breakthrough [min]	*Rating
Best Glove	N-DEX 7005	Nitrile	4 mil	30	Poor
Best Glove	N-DEX 8005	Nitrile	8 mil	45	Poor
Best Glove	Nitri-Solve 727	Nitrile	15 mil	60	Fair
North	LA102G	Nitrile	11 mil	60	Fair
Ansell	Chemi-PRO 224	Neoprene/latex blend	27 mil	153	Good
Best Glove	Chloroflex 723	Neoprene	24 mil	180	Good
Best Glove	Best Viton 890	Viton	28 mil	185	Good
Ansell	Canners 392	Natural rubber latex	19 mil	190	Good
Best Glove	SOL-VEX 37-165	Nitrile	22 mil	334	Good
North	PNLB1815	Natural Rubber	18 mil	420	Good
Ansell	Neoprene 29-865	Neoprene	18 mil	>480	Good

Best Glove	Best Butyl 878	Butyl	25 mil	>480	Good
Ansell	Barrier 2-100	Laminated LCP- Film	2.5 mil	>480	Good
North	SSG Silver Shield	Silver	2.7 mil	>480	Good

### Engineering Controls

- Stock solutions of concentrated HF (~49%) limited to 500 mL containers.
- Secondary containers are available for transportation
- An inspected designated fume hood is used
- The fume hood sash is used to protect the face and upper body when face shield is not in use
- A warning sign alerting laboratory users of the presence of HF is posted
- Incompatible materials were removed from the hood

## **Section 3: Procedures**

### Silicon Etching Procedure

1. Put on PPE.
2. Separate the top and bottom halves of the etching cell.
3. Remove etching cell from food hood and put it on a lab towel in the designated HF workstation.
4. Place silicon sample on (platinum?) plate on lower half of the etching cell.
5. Tape the very most corners of the silicon sample down using scotch tape.
6. Turn top half of the etching cell upside down and secure the O-ring in the circular groove.
7. Turn the bottom half of the cell upside down, and assemble the etching cell by connecting the bottom and top halves together.
8. Check that the O-ring is in place, then screw the screws to tighten the contact between the top and bottom halves of the etching cell.
9. Bring the cell to the fume hood, and connect the counter electrode to the bottom screw on the cell.
10. Use the approved plastic tweezers to take the magnetic stirrer out of the waste container funnel, and place it in the cell. Turn the stirrer onto the minimum setting.
11. Put the electrode into the cell, about 0.5-2 cm below the surface of the HF, in the center of the cell.
12. Carefully open the HF container inside of the fume hood, and pour the HF into the cell. Then close the now empty HF container.
13. Close the fume hood, turn off the fume hood light, and apply the appropriate current using the potentiostat.
14. On the potentiostat, set the pulse time to 0.25 seconds, set the number of loops to 4, and set the number of pulses to number of desired etching seconds minus one.
15. Once the etching is done, turn on the fume hood light, open the fume hood, turn off the stirrer, and remove the electrode.
16. Use the polyethylene pipette to return the HF to its container, tightly sealing the container.
17. Remove the counter electrode from the bottom of the cell.
18. Pour ethanol down the side of the cell until the bottom of the cell is filled.
19. Empty the ethanol into the waste container.

20. Repeat steps 18 and 19.
21. Blow the inside of the etching cell dry with nitrogen gas inside of the fume hood.
22. Disassemble the cell and remove the etched silicon sample.

#### Section 4: Spill Cleanup

- Verify that a spill kit is readily available before working with HF. Note that commercial spill kits are available, but **MUST** be rated specifically for HF use—not just general acid use. The use of solid calcium carbonate is recommended to absorb HF spills. Calcium will form an insoluble salt with fluoride and prevent fluoride absorption through the skin. **DO NOT** use sand, as HF reacts with it to form toxic tetrafluorosilane. The spill kit should also contain: A plastic container with lid or heavy duty plastic bag to collect any contaminated material, gloves resistant to HF, dust pan and broom. Spills inside the fume hood should be neutralized immediately and the area cleaned up thoroughly after neutralization. Ask for assistance if you do not feel confident that you can perform the clean-up adequately.
- In the case of a spill outside the fume hood that cannot be neutralized safely, evacuate the area immediately and alert others. If possible, close the door to prevent vapors from spreading to other spaces and call 911 immediately. In the case of splashes on clothes, gloves, or shoes with no contact to skin, remove the item carefully, avoiding contact to skin. Put the items into a heavy-duty plastic bag and then seal and label the bag. Wash the affected skin area with soap and water even if no skin contact is evident.

#### Section 5: HF Storage

- HF should be stored in a cool, dry area, well ventilated area out of direct sunlight.
- All HF containers and holders should be labeled clearly and precisely.
- HF should only be contained within polypropylene containers in Beckman Institute.
- HF bottles should be stored in a secondary container in the lowest available cabinet space.
- Calcium carbonate can be contained within the secondary container to neutralize any spilled HF.

#### Section 6: Waste Disposal/Cleanup

- When your work with HF is done, collect spent and excess solution as HF waste. Aqueous HF waste solutions should be collected in polypropylene containers and labeled accordingly. They can be disposed of through the DRS chemical waste (<http://www.drj.illinois.edu/regwaste/pdf/WasteDisposalGuide.pdf>).
- Rinse used and emptied containers with a small amount of water and add the rinsing solution to the HF waste. The containers can then be rinsed thoroughly with soap and water.
- Disposable equipment that is contaminated, and reusable equipment that is contaminated and cannot be safely decontaminated, should be discarded. Put the contaminated item into a plastic bag and label it “debris contaminated with hydrofluoric acid”. HF-contaminated debris can be disposed of through the

DRS chemical waste program under UI number 50038 according to the UIUC Chemical Waste Management Guide (<http://www.dr.illinois.edu/regwaste/pdf/WasteDisposalGuide.pdf>).

## Section 7: Emergency Response

- Administer the appropriate first aid and call 911 immediately upon contact with HF. First aid should be administered and 911 should be called even if no pain is felt. The onset of HF exposure symptoms can take up to 24 hours (See “Health Effects” under “Hazardous Conditions” subsection of Section 2).
- **Skin** Remove contaminated clothing, shoes, and leather clothing or accessories immediately upon exposure. Wash with lukewarm water for 5 minutes and apply 2.5% calcium gluconate gel to affected areas immediately. Call 911 immediately.
- **Eyes** Call 911 immediately. Immediately flush eyes with lukewarm water for 15-20 minutes if eye contact is made. Do not attempt to remove contacts if you wear them. If 1% calcium gluconate solution is available, wash eyes with water for 5 minutes and then repeatedly rinse eyes with 1% calcium gluconate solution.
- **Ingestion** Call 911 immediately. Do not swallow anything. Do not induce vomiting. Thoroughly rinse mouth with water. If natural vomiting occurs, rinse mouth again.
- **Inhalation** Call 911 immediately. Move to fresh air. Do not move around unnecessarily. CPR or AED may need to be administered if breathing or heart stops.

## Section 8: Safe Handling of HF

- Limit stock solutions of concentrated HF to 49% and limit to 500 mL containers. Contact superuser if anything varying from this is desired
- Only open one bottle of HF at a given time
- Don't use more HF than needed
- Let someone else know when you are using HF. Do not use HF when alone in the lab
- Never transport any open HF containers. Always use a secondary container when transporting HF long distances
- Only use HF in a designated chemical fume hood
- Post a warning sign so that other lab users are aware which chemical fume hood is designated for HF use
- Do not put incompatible materials in the hood with HF (Glass, metals, strong bases, alkalis, silica, cyanides, carbonates, reducers, and ceramics are all incompatible with HF)

## Section 9: Additional Information

### Advice:

- HF vapors may be inhaled when aligning the electrode for silicon etching. An electrode must be aligned above the silicon etching cell when HF etching. Align the electrode before pouring the HF into the etching cell.
- Only use HF if you have a clear mind, good mental health, and are not tired or sick.
- Check gloves for HF splashes whenever possible.
- Only hold the HF container caps by the sides.

- Inspect the sample after loading into the etch cell to ensure the O-ring is in place and no openings are visible.
- Move slowly, carefully, calmly, and confidently when using HF.

Checklist:

- Read (Material) Safety Data Sheets.
- Receive training from another experienced HF user (Corey Richards or Christian Ocier).
- Another researcher is nearby and knows the hazards present.
- All calculations are done prior to beginning the procedure.
- Proper PPE and engineering controls are in use.
- You are not tired or sick and are in a good mental state.
- Calgonate gel is nearby and not expired.
- A charged phone is nearby in the case that emergency personnel need to be contacted.
- The waste container is not full and the ethanol bottle is not empty.

References:

OSHA Chemical Sampling Information: Hydrogen Fluoride

[https://www.osha.gov/dts/chemicalsampling/data/CH\\_246500.html](https://www.osha.gov/dts/chemicalsampling/data/CH_246500.html)

NIOSH Pocket Guide to Chemical Hazards: Hydrogen Fluoride

<http://www.cdc.gov/niosh/npg/npgd0334.html>

EPA Air Toxics Website

<https://www.epa.gov/haps/health-effects-notebook-hazardous-air-pollutants>

Centers for Disease Control and Prevention (CDC) Fact Sheet

<https://emergency.cdc.gov/agent/hydrofluoricacid/basics/facts.asp>

DRS Safety Library

<https://www.drs.illinois.edu/SafetyLibrary/HydrofluoricAcid>