



Standard operating procedure for hazardous chemicals

HF solution etch

The content of this document was edited by Raluca Gearba

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Risk Assessment

Hazardous Chemicals: *(List chemicals used. Include chemical name, common name and abbreviation)*

Hydrofluoric acid is a clear, colorless liquid.

- It is an extremely dangerous material and all forms, including vapors and solutions.
- HF can cause severe, slow-healing burns to tissue.
- Reaction to contact may be delayed. At solutions of 20%, burns may not become noticeable for hours.
- HF readily penetrates skin, damaging underlying tissue.
- The fluoride ion can then cause destruction of soft tissues and decalcification of the bones.
- HF can cause severe burns to the eyes, which may lead to permanent damage and blindness.

Chemical approved for use in the Cleanroom HF hood

- 1) *Buffered oxide etchant (BOE), Buffer HF improved, solution UN2817, Transcene (mixture of ammonium hydrogen difluoride, hydrofluoric acid and water)*
- 2) *Hydrofluoric acid (48 wt. %), 7667-39-3*

Potential Hazard(s): *(Describe the potential hazards associated with the chemicals or the procedure.)*

HF has many potential physical and health hazards. A less hazardous solution/process should be used if possible.

- 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.
- Calcium gluconate gel will bind to the fluoride ions and prevent further tissue destruction, but it must be applied quickly (even if burns have not been felt) to be effective. Calcium gluconate gel information is found at: http://www.calgonate.com/calgonate_gel.php
- Consult the Safety Data Sheet (SDS) for your specific product and the Laboratory Chemical Safety Summary for HF in *Prudent Practices in the Laboratory* (National Academies Press).

Routes of Exposure: *(As applicable, describe the potential routes of exposure associated with the procedure such as inhalation, injection, skin/eye contact)*

People working in areas where hydrofluoric acid is used should be familiar with these guidelines and they should be readily available (printed out) and kept with first aid supplies.

During regular business hours call the HealthPoint Occupational Health Program at 512-471-4647 for medical advice on occupational chemical exposures.

For an actual chemical exposure/injury

- Seek immediate medical attention at the emergency department for any HF exposure.
- Persons helping an exposed colleague must wear PPE as indicated below.
- Call 911 from a campus phone or from any phone to request assistance and/or emergency transport, if needed. EOHW or EMS personnel may recommend administration of calcium carbonate tablets (such as Tums) for skin exposure.

When calling remember to have your name, phone number, location, and any other pertinent information available at the time of the call. It is important to inform the safety office and the police if anyone has been injured or if there has been a personal exposure.

For skin exposure:

- If using calcium gluconate gel (2.5%), flush with water for 15 minutes then apply the gel by rubbing onto the burn site. Continue to massage the calcium gluconate gel into the burn site during transportation to a medical facility and while waiting to see a physician. The person applying the calcium gluconate gel should wear acid resistant gloves (neoprene, 30 mil thick) to prevent a secondary HF burn. If not using calcium gluconate gel, continue rinsing with water until medical treatment can be provided.

For 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, after which the calcium gluconate solution (1%) should be used repeatedly to irrigate the eye using a syringe.
- Take the victim to a doctor, preferably an eye specialist, as soon as possible. Use ice water compresses on the eyes during transportation.

For ingestion:

- Administer a calcium-containing medication (such as Tums), if available. Magnesium-containing stomach medication or several glasses of milk may also be given. Get immediate medical attention.

Quantity/Concentration Hazards: *(As applicable, describe if the quantity/concentration of the chemical increases the risk associated with exposure to the chemical.)*

- 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.

Substitution of Less Hazardous Chemicals: *(As applicable, describe the potential use of less hazardous chemical substitutes)*

HF solutions should only be used when necessary. Try to avoid using it if a less reactive agent works.

Contact EHS lab safety staff at 512-471-3511 for a possible alternative.

Control Measures

Personal Protective Equipment (PPE): *(List all applicable personal protective equipment needed for procedure)*

Wear a fully buttoned lab coat with sleeves extended to wrists, face shield AND safety goggles, neoprene acid resistant (30 mil thick) outer gloves and nitrile inner gloves, long pants (or other clothing covering the entire leg), rubber apron, and closed toed shoes.

Engineering Controls: *(As applicable, describe the engineering controls used for the procedure)*

- Any work with HF must be done in a chemical fume hood.
- An eyewash unit must be available in the immediate work area.
- A small supply of appropriate neutralizer for spills should be kept near the fume hood where the work will be conducted.
- No work with concentrated HF should be performed alone. A second person with knowledge of the dangers and emergency procedures for HF contact must be present at all times within the laboratory while the operations with HF are being carried out.

Work Practice Controls: *(As applicable, describe work practice controls used for the procedure)*

- Consider alternate methods and use a less dangerous acid, if possible.
- Purchase HF in the smallest amounts possible.

- Stock calcium gluconate gel and calcium carbonate antacid tablets (Tums) to be used as first aid in case of an HF burn. (Medical attention should still be sought immediately for HF burns.) Prior to using HF, make sure the calcium gluconate tube is unopened and that neither the gel nor the tablets have reached their expiration date.

The HF First aid kit is stored on the wire rack to the left of the HF hood in the cleanroom.

- Do not heat hydrofluoric acid.
- Do not use glass, ceramic, or other incompatible containers for HF.
- Perform a dry run to identify and correct potential hazards.
- Work within sight and/or hearing of at least one other person who is familiar with the hazards and written procedures.
- Set up a designated area for HF use and post a warning sign during use.
- Use containment tray of compatible material.
- Once work with HF is complete, decontaminate the area by wiping it down with the provided HF acid eater solution.

Monitoring: *(As applicable, describe any monitoring needed for the procedure)*

Non applicable

Use in Animals: *(As applicable, describe how the chemical will be safely used in animals)*

Non Applicable

Cleanup Procedures: *(Describe the process for cleaning the work area during and after the procedure.)*

- At the end of the procedure all beakers, Teflon funnel and surfaces need to be cleaned with water and dried.
- The waste solution should be disposed of in accordance with the procedure described below.

Storage Procedures: *(Describe how and where the chemical will be safely stored)*

- Store in a compatible container (preferably polyethylene). HF reacts with glass, ceramics, and some metals.
- Place it in a compatible secondary container to capture leaks or spills.
- Store with other inorganic acids, away from bases and other incompatibles including metal (unless the metal has a corrosion-proof coating), and do not store under the sink.
- Avoid storing on the floor.
- Store away from incompatibles.

Transportation Procedures: *(If the chemical will be transported on campus, describe procedure)*

- Transport corrosives in secondary containment, preferably a polyethylene or other non-reactive acid/solvent bottle carrier.

Waste Disposal Procedures: *(Description of how waste will be disposed)*

- Before using HF solution make sure you have available a suitable waste container. The container must be HF compatible (preferably polyethylene). HF reacts with glass, ceramics, and some metals.
- The waste container must have attached to it and EHS waste tag with the following info (name, phone number, location, description of the content and amount)
- Store the waste containers under the dedicated HF hood.
- When the processes are done, take the container and place it on the dedicate Teflon tray in the hood. Have a Teflon funnel available to pour the HF solution into the waste container
- Contact the TMI staff to dispose of the waste when the container is 2/3 full

Emergency Procedures: *(Describe what procedures should be followed in the event of an emergency)*

Spills or Releases: *(Provide specific instructions on what personnel should do in the event of a spill or gas release. Include location of spill kits.)*

- Spills of HF in the fume hood (<5 ml) should be cleaned using the provided HF acid eater solution. After neutralization rinse with water.
- Keep spill cleanup materials at locations where the solutions are prepared. The spill kit should be located no further than 3ft from the dedicated HF hood. If a spill occurs notify the TMI staff and your supervisor immediately.

Fire: *(Provide specific instructions on what personnel should do in the event of a fire)*

In case of an extensive fire evacuate the building and then call 911 immediately. Inform the TMI staff and your supervisor.

In case of a small fire and if properly trained use the fire extinguisher located to the right of the acids hood. Inform the TMI staff and your supervisor.

Emergency Shut Offs: *(If applicable, describe procedures for shutting down equipment in an emergency)*

In case there is a need to leave the area because of an emergency please leave the sign “HF solution in use” sign on the hood in clear view

Signs and Symptoms of Exposure: *(Describe the specific signs and symptoms of an exposure to the chemical)*

In the HF concentration is lower than 20% there might be no signs. Be aware that symptoms can be delayed. In any case, if you come in contact with or believe you have come in contact with HF follow the procedures below.

Exposures: *(Provide specific instructions on what personnel should do in the event of an exposure)*

Skin Exposure:

- NOTE: All HF exposures should be reported to EHS and OHIP.

- Move the victim immediately under an emergency shower or other water source and flush affected area with large amounts of cool running water for at least 5 minutes. Clothing, shoes and jewelry should be removed while the water is flowing on to the victim.
Goggles should be removed last while the victim is facing the water flow. Colleagues must be EXTREMELY CAREFUL not to become contaminated while assisting the victim.
Neoprene acid resistant gloves (30 mil thick) should be worn.
- While the victim is being rinsed with water, call 911 and inform the emergency dispatcher of the exposure and request emergency transport. Ensure emergency responders and treating physicians are aware of the nature of the chemical exposure. Provide a copy of the MSDS to emergency responders.
- After the affected area is flushed with copious amounts of water for at least five minute, apply 2.5% calcium gluconate gel according to this procedure. Massage gel into affected areas. Flush skin surfaces with water for at least 15 minutes if calcium gluconate gel is not available. In order to prevent cross contamination, the victim should self-apply the calcium gluconate gel. If the victim is unable to self-apply, anyone present can apply the gel after first putting on thick neoprene or nitrile gloves. Do not use latex gloves because they are not an effective barrier against HF. Note the time when the calcium gluconate gel was first applied to the contaminated skin and provide this information to the emergency responders. Re-apply gel every 15 minutes until medical assistance arrives.
- After the emergency responders arrive they will call the Emergency Room doctor for instruction and may administer the calcium carbonate tablets (antacid tablets) in the Spill Exposure Kit.

Eye Exposure:

- Immediately flush eyes for at least 15 minutes with copious cool flowing water. Call 911, inform the emergency dispatcher of the exposure and request emergency transport. The victim should then be transported to a medical facility. Apply a sterile 1% calcium gluconate solution to the victim's eyes after irrigation. If this solution is available the washing can be reduced to 5 minutes.
- Ensure emergency responders and treating physicians are aware of the nature of the chemical exposure. Provide a copy of the MSDS to emergency responders.

Inhalation:

- If a large amount of Hydrofluoric Acid gas is inhaled, immediately remove the victim to clean air. Call 911, inform the emergency dispatcher of the exposure and emergency transport
- Ensure emergency responders and treating physicians are aware of the nature of the chemical exposure. Provide a copy of the MSDS to emergency responders.
- Inhalation of Hydrofluoric Acid fumes may cause swelling in the respiratory tract up to 24 hours after exposure. Persons who have inhaled Hydrofluoric Acid vapors may need prophylactic oxygen treatment and must be seen by a physician as soon as possible.

Occupational Health Requirements: *(Describe any Occupational Health requirements necessary that are associated with the procedure. Examples include medical evaluation, baseline serum samples and respiratory fit testing)*

There is no specific evaluation required prior to the use of this specific procedure

Material Safety Data Sheets (MSDS): *(Describe how personnel will access MSDS in the lab. Include a copy of the MSDS with this SOP)*

The MSDS for the HF and BOE solutions are attached to this SOP and also stored in a holder outside of the cleanroom in the viewing area.

Training Requirements: *(Describe what training personnel must complete before using chemical/procedure. This training should be documented)*

The users must complete the General Cleanroom safety training (has as requirement the OH101 OH201 courses)

Review of Procedure: *(Describe the frequency for reviewing the SOP document)*

The present SOP will be reviewed every 6 months.

Protocol:

Description of how to safely perform the experiment or operation.

- Prepare the samples for the etch cycle and place them in a Teflon basket with a lid and a lowering rod.
- Put on the acid-resistant apron, neoprene acid resistant gloves (30 mil thick), safety goggles and face-shield before starting the process. Please inspect the acid resistant gloves before each use.
- Pour 500 ml of the Buffered HF solution into an HDPE/Teflon beaker, keeping the beaker in the sink.
- Fill another HDPE/Teflon beaker with DI water from the tap, and keep the tap running over the beaker to supply fresh water during the etch cycle.
- Fill a second HDPE/Teflon beaker with DI Water and move it to the smaller sink.
- Dip the Teflon basket assembly in DI water for 10 seconds then lower it gently into the HF beaker, without splashing the acid out.
- After the etch-time has elapsed, slowly take the basket out of the beaker and drip off excess acid back into the beaker.
- Then transfer the basket over to the “running water” beaker and let it sit inside for at least 30 seconds.
- Slowly remove the basket from the beaker, rinse the entire assembly with the DI water gun and place it in the “stagnant water” beaker for another 30 seconds.
- Dry the samples and removed from the hood.
- Once the etch is done, very carefully pour the used HF solution into a waste-bottle with the help of a Teflon funnel. This process should be done inside the sink or the large tray.
- Thoroughly wash every item used in the process with water, and triple-rinse all the beakers.
- Triple rinse gloves with water gun before removing them.

Report any encountered problems to Raluca Gearba at gearba@austin.utexas.edu

“I have read and understand this SOP. I agree to fully adhere to its requirements. By signing below, I also acknowledge that I have received hands-on training for use of HF solutions.”

Date	User name	Eid	Signature	Trainer initials