Standard Operating Procedure for Hydrofluoric Acid and Buffered Oxide Etch

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| Department: | Choose a department.  Enter department here if not listed. |
| Principal Investigator: | PI name. |
| Group Safety Coordinator/Lab Manager: | Name of safety contact. |
| SOP written by:  *All author’s names should be recorded in “Changes” section.* | CoE SOP Committee  jorawiec@illinois.edu |
| Date of this version of the SOP:  *Dates of revisions should be recorded in “Changes” section.* | Click here to enter the date of this version of the SOP. |
| Date SOP was approved by PI/lab supervisor: | Click here to enter date SOP was approved. |
| Lab Phone: | Enter the lab phone number |
| PI’s Phone: | Enter the PI office or mobile phone number |
| Location(s) covered by this SOP: | Enter the building and room number |
| Emergency contact information for this location: | Enter contact information of lab personnel to be notified in case of emergency. |

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| Type of SOP: | Hazardous material  (SOP describes a specific hazardous chemical) | Hazardous class  (SOP describes a group of hazardous materials ) | Hazardous Process  (SOP describes a hazardous process or equipment) |

**NOTE**: This SOP is intended as an initial resource and as a general reference regarding the topic discussed. It is not a substitute for hands-on training and supervision by experienced laboratory personnel. The Principal Investigator must review and approve of all information in this document for the SOP to be valid and useable.

*This SOP is not complete until: 1) Clear and detailed instructions are written that will ensure safe handling of the material or safe performance of the procedure, and 2) SOP has been approved and dated by the PI or laboratory supervisor.*

Print a hardcopy and insert into your *Laboratory Safety Manual* and *Chemical Hygiene Plan*.

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# Purpose

These safe handling guidelines describe standard procedures to be observed when handling hydrofluoric acid (HF) and buffered oxide etching solutions in research laboratories.

These guidelines are intended to function as an initial resource and as a general reference for safe handling of HF-containing materials. The use of this SOP as a training tool is encouraged, however, it is not a replacement for personal hands-on training and supervision by experienced laboratory personnel, nor does it avoid the need to ascertain specific details concerning the safe handling of hydrofluoric acid before use. Research laboratories needing to make lab-specific changes to these guidelines should edit this document however they deem necessary to suit their needs. The edited document should then be placed in the research group’s laboratory safety plan, with training being documented. *Principal investigators must approve of all edits before they are accepted into this document*.

# Key Points

* **Always remember that hydrofluoric acid is not only corrosive but highly toxic!**
* **Always have calcium gluconate kit (HF exposure kit) readily available before working with hydrofluoric acid. Be sure it hasn’t expired.**
* Know what personal protective equipment will protect you against exposure to HF–your life may very well depend on it!
* Know the locations of the nearest emergency shower, eye wash and sink. The ability to quickly wash off spills is imperative in protecting your health and well-being. **The availability of nearby emergency showers, eye washes and calcium gluconate gel is a must for working with fluoride-ion-containing materials!**
* Always thoroughly clean the equipment and the work area when finished working with hydrofluoric acid to prevent chemical exposures from accidental contact.
* Know how to clean up a spill of HF before working with it.
* Know how to safely store HF and know what materials it is incompatible with. This is also very important during storage prior to disposal. **Store acids separately from bases!**
* As much as possible, work with HF in a chemical fume hood.
* Stir hydrofluoric acid slowly. When dilution is necessary, always carefully add hydrofluoric acid to water, to limit the rate at which heat is released. If done in the reverse, enough heat is often generated to cause splattering of concentrated hydrofluoric acid.
* When acids attack metals, hydrogen gas can be released. Hydrogen gas can burn or explode if an ignition source is present.
* Hydrofluoric acid and some fluorides etch glass and should not be used with or stored in glass.
* This SOP **does not** cover the use of HF gas supplied in cylinders. This gas is also toxic and requires the use of a vented gas cabinet (discussed in another SOP).

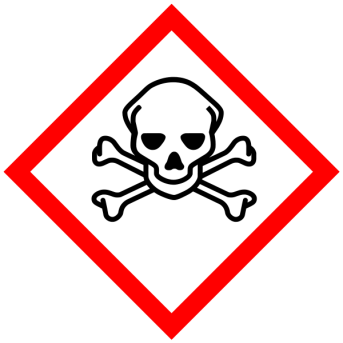
# Hazard Awareness

## Definition of terms

Hydrofluoric acid (HF) is most commonly available as an aqueous solution. Up to 49% HF, it is a non-fuming, corrosive acid of pH 3.4. Higher concentrations of HF produce fumes. Buffered oxide etch (BOE), also known as buffered HF or BHF, is a solution of ammonium fluoride and hydrofluoric acid. The concentration of BOE varies and is often specified as the volume ratio of 40% NH4F in water to 49% HF in water. For example, 6:1 BOE is 6 parts 40% NH4F to 49% HF. Fluoride salts such as sodium fluoride (NaF) and ammonium hydrogen difluoride (NH4HF2) are available as powders. Solutions of fluoride salts often have similar toxicity characteristics as hydrofluoric acid. The likely route of exposures would be inhalation of HF fumes and dermal or eye contact with solutions and powders. Researchers utilizing hydrofluoric acid and fluoride salts **must** read and understand the manufacturer’s Safety Data Sheet (SDS) prior to commencing work with such materials.

Characteristics of hydrofluoric acid include:

* May cause death or serious bodily harm.
* Has a low pH and LD50\*
* Has the following GHS symbols;



* May react with incompatible chemicals to produce heat and/or flammable & toxic gas.
* Hydrofluoric acid reacts with:
  + Metals
  + Bases (caustics)
  + Silicon-containing compounds (glass, ceramics, etc.)
  + Azides, cyanides, bleach and sulfides
* May cause burns upon contact with skin. Onset of visual symptoms may be delayed by hours.

\*LD50/LC50 definition (Merriam-Webster)

The amount of a toxic agent (as a poison, virus, or radiation) that is sufficient to kill 50 percent of a population of animals usually within a certain time.

## **Hazards and pertinent regulati**ons

HF produces tissue damage via two mechanisms. First, free hydrogen ions cause corrosive burns. Second, fluoride ions penetrate the tissue and cause chemical burns by forming insoluble salts with calcium and magnesium in the body. Fluoride ions combine with other cations to make soluble salts that dissociate quickly. As a result, fluoride ions are released again, causing further tissue destruction/necrosis. Unlike other acids which can be rapidly neutralized, the neutralization of HF may require days, during which tissue destruction may continue. HF binds with calcium whenever it contacts skin or other tissues. Because calcium is required for cell life, this calcium-binding may result in rapid cell death. Extensive HF exposure can inactivate large amounts of calcium in the body, significantly depleting calcium supplies required for vital bodily functions.

If left untreated or undertreated, minor exposure may produce the same severe consequences as high-concentration HF burns. The delayed onset of symptoms may lull patients and medical caregivers into believing that the exposure did not cause harm, prolonging exposure and delaying treatment. Moreover, deterioration can be precipitous – patients with minimal symptoms can progress suddenly to ventricular arrhythmia and even death.

Because of this calcium-binding effect, the most serious consequences of exposure to HF are hypocalcemia and hypomagnesemia, the lowering of serum calcium and magnesium, respectively, which can result in complete heart failure. Although flushing the affected area is effective in removing surface acid, it doesn't affect the fluoride ions that may have already penetrated. Cell destruction and bone demineralization may progress for several days.

## Means to control the hazards

Minimizing exposure is very important when working with HF. The use of engineering controls and personal protective equipment (PPE) is necessary. Proper storage of HF must be followed. The key to ensuring safety is to recognize and be aware of HF’s toxic and corrosive properties, assess the risk of exposure (i.e., how you might be exposed in the course of your work/process using these reagents), minimize the hazard through the use of engineering controls and PPE, perform the appropriate procedures, prepare for spills and splashes of HF by ensuring the availability of the necessary safety equipment, and to have a rehearsed plan to deal with emergencies.

## Examples of hazardous materials or processes

*PI’s and Lab managers: enter HF-containing materials used in your lab in this section.*

# Important considerations

## **Prior approval from PI required?**

Yes

## Consultation of other reference material, documents or knowledgeable persons required?

The Division of Research Safety website has information on [hydrofluoric acid](https://www.drs.illinois.edu/SafetyLibrary/HydrofluoricAcid) that may serve as useful reference information.

## Pre-requisite training or skill?

Corrosive materials and DRS HF training ([online](https://www.drs.illinois.edu/Training?section=ChemicalSafety#HydrofluricAcidTraining))

## Experiment Risk Assessment required?

Consult this link: [Risk Assessment for Chemical Experiments](http://www.drs.illinois.edu/site-documents/RiskAssessmentWorksheet.docx)

Enter any required risk assessment step or procedure.

## Other important considerations:

Any special First Aid concerns? Any special tips or tricks?

# **Emergency response**

## Introduction to emergency response

Skin and eye exposure is the most likely hazard associated with HF. Inhalation is another likely hazard if vapors, fumes, or mists are encountered. While prevention is key, ample preparation for emergencies is necessary. Examples of such preparation include making sure emergency showers and eyewash are operating properly, and that spill kits are stocked to deal with spills. Spill response requires taking the necessary steps to avoid contact or exposure to the hydrofluoric acid during clean up. Clean up should be followed by proper storage and disposal of the waste.

## Necessary emergency equipment

**Spill Kit for HF**

An ideal spill kit for HF should be composed of the following;

* Chemically resistant gloves
* Sealable plastic bags
* 3-5 kg of acid neutralizer (calcium carbonate or commercial HF neutralizer) \*
* Dust pan and whisk broom
* 5-gallon plastic pail

Place all listed materials in the 5-gallon pail and label the pail “HF Spill Kit”. Place spill kit in an easily accessible location that is known to all lab personnel.

\*Neutralizing hydrofluoric acid with sodium bicarbonate will produce a highly toxic and water soluble compound (sodium fluoride). Neutralizing with **calcium carbonate** powder (or commercial products such as “HF Eater”) will produce a water-insoluble compound (calcium fluoride), rendering the fluoride harmless.

**Emergency shower and eye wash**

Emergency showers and eye washes are needed wherever there is a possibility of exposure to hydrofluoric acid. An emergency shower/eyewash that provides a 15-minute flush of the eyes and body should be located within 10 seconds walking distance (about 55 feet) of the area where work is being performed. Keep the path to emergency equipment clear.

**Exposure kit for HF**

To be prepared for handling an HF exposure incident, it is recommended that an exposure kit be available. This kit should contain calcium gluconate gel and a hardcopy of the SDS of HF/BOE. The SDS should be presented to the attending physician who is providing treatment to the exposed person. Calcium gluconate 2.5% topical gel must be made available if hydrofluoric acid (HF) work is being conducted. Be sure to check the expiration date to make sure it has not expired. Prophylactic use of calcium gluconate gel (applying it to hands as a preventative measure prior to working with HF) is NOT recommended as this depletes the stock of gel available for emergency use.

## What to do if there is a spill or a fault in the process.

**IMPORTANT NOTES:**

**Before work begins** – You must know how to clean up any spill or leak of a material before working with it! You should be aware of the location of emergency equipment before commencing clean up.

**Comfort level** – If the person faced with cleaning up the spill or their supervisor feels that it is too large to safely clean up, he or she instead should proceed as described in **Large/Complicated Spill** section below.

**SPILLS**

**Small/Simple Spills**

To use spill kit, first don personal protective equipment (PPE) that includes chemically resistant gloves, lab coat, and safety glasses. If corrosive material is:

* **Solid –** use whisk broom and dust pan to carefully clean up the fluoride solid. Then place material in plastic bags or pail.
* **Liquid** – sprinkle the appropriate neutralizer on all surfaces exposed to the corrosive material until the material stops reacting to the neutralizer. Let stand for 5-10 minutes and then proceed to clean up the spill by placing the material in plastic bags or pail.

Seal the waste bags or pail and store in a safe manner until chemical waste personnel pick up the material. Carefully and thoroughly wash spill area with soap and water. Dispose of all soiled spill material through the University of Illinois chemical waste management program (see **Waste disposal** section).

**Large/Complicated Spills**

If an unmanageable spill of corrosive material happens;

* Inside the fume hood - close the sashes of the chemical fume hood.
* Outside the fume hood – open the sashes of the chemical fume hood (to evacuate corrosive vapors) and cordon off the area where spill occurred.

In either case, immediately evacuate the laboratory and call 911 to alert emergency responders.

## What to do if there is an exposure or injury

**FIRST AID**

**Note:** *If HF exposure is suspected, follow the first aid procedures* ***immediately****. A visit to the Emergency Room is necessary, even if there are no apparent symptoms. Bring the SDS with you to show the attending physician.*

The first thing to do is to rinse exposed areas with large quantity of water for 15 minutes. Skin exposure must then be treated by application of 2.5% calcium gluconate gel. Eye exposure will require the *immediate* use of an eye wash. Seek medical assistance regardless of extent of exposure. Get help from a lab mate. If no one is available to help you, **call** **911 immediately**. **Seek emergency medical care without delay**\*.

**Third party:** Assist the victim. Seek medical assistance\*. In case of life-threatening situations (impaired or loss-of consciousness, difficulty breathing, etc.) **call 911 immediately**! Stay with the victim. If possible, ask another person to meet responders so that they can find you quickly. If possible, ask another person to meet responders so that they can find you quickly.

\* See the Division of Research Safety guidance document [Medical Treatment Options](http://www.drs.illinois.edu/AccidentResponse/MedicalTreatmentOptions) for more information.

*PI’s and Lab managers: enter first aid information for specific hydrofluoric acid used in your lab in this section. Document not valid until filled in.*

# Storage

## Considerations for safe storage of materials

Hydrofluoric acid must be stored:

* With appropriate warning labels and placards.
* With containers kept inside secondary containment or a spill tray, such as a plastic bin. The secondary containment must be big enough to hold a spill volume amounting to the total of volume of containers stored in it, with room to spare.
* According to manufacturers’ SDS, in approved containers, inside an approved storage cabinet.
* With quantities kept to a minimum.
* In a compatible manner with other reagents. **IMPORTANT:** Always store hydrofluoric acid away from silicon containing materials (glass, ceramics, etc.), metals, bases (caustics), azides, bleach, cyanides, and sulfides!



**Figure 1.** Example of hydrofluoric acid storage – note the calcium carbonate powder in secondary containment to neutralize HF that may drip down sides of bottles.

## Quantity limits and other considerations

Specify applicable regulatory or self-imposed storage quantity limits.

# Work Practices and Engineering Controls

## Introduction to work practices and engineering controls

* All reactions utilizing hydrofluoric acid must be done in a properly operating chemical fume hood, glove box or appropriate engineering control with emergency spill kits accessible and nearby.
* Be sure all equipment being utilized is compatible with hydrofluoric acid. Glassware is not compatible with hydrofluoric acid.
* De-clutter and remove from the work area any incompatible material that is not necessary.
* The manipulation of hydrofluoric acid should utilize locking mechanisms (luer locks, etc.) and have apparatus connections clamped (keck, etc.) when appropriate.
* Inexperienced users of hydrofluoric acid must be supervised while performing experiment.
* To prevent spills, don’t fill vessels near their maximum capacity.
* Have reaction apparatus staged/set up before transferring hydrofluoric acid to it.
* Always thoroughly clean equipment and the work area when finished to prevent chemical exposures from accidental contact with hydrofluoric acid. This also helps to prevent damage and corrosion to equipment.

## Designated area to work with the material or process

A thorough risk assessment will determine the appropriate work area where the specific procedure may be carried out. An important consideration is the availability of a nearby emergency eyewash and shower.

## **Necessary engineering or administrative controls.**

If necessary, consult the [Campus guidance on use of chemical fume hoods](https://www.drs.illinois.edu/SafetyLibrary/ChemicalFumeHoods).

All experiments utilizing hydrofluoric acid should be done in a properly operating chemical fume hood or appropriate engineering control with nearby emergency spill kits. Hydrogen Fluoride is also classified as toxic and must be kept in a vented gas cabinet*. The use of Hydrogen Fluoride gas is outside the scope of this SOP.*

## **Required Personal Protective Equipment (PPE).**

If necessary, consult the [Campus guidance on personal protective equipment.](https://www.drs.illinois.edu/SafetyLibrary/PersonalProtectiveEquipment)

Fully enclosed shoes (no holes in the top) must be utilized when manipulating hydrofluoric acid. Long hair should be tied back and full-length pants or skirts must also be worn along with basic PPE to include:

* **Eye protection –** Safety glasses meeting American National Standards Institute (ANSI) standard Z87.1 are required while manipulating hydrofluoric acid. If a splash hazard is present, a face shield may be required in addition to safety glasses.
* **Gloves –** Gloves are required at all times. Glove choice should balance the need for dexterity and chemical resistance. Select the glove for compatibility with the material being handled.
* **Lab coat –** Chemical resistant, knee-length lab coats that are buttoned up are required.
* **Apron or smock –** A suitably-resistant apron or smock can offer protection from splashes.

# Detailed procedures or techniques

## Step-by-step procedures

**LIQUIDS**

When manipulating hydrofluoric acid, pay attention to three considerations: Ventilation, PPE and thorough cleaning. Ventilation and PPE are of critical importance to reduce exposure to hydrofluoric acid and must be used whenever possible. Once the manipulation of hydrofluoric acid is completed, a thorough cleaning of all equipment and lab space (e.g. containers, counter tops, etc.) is prudent to reduce chemical exposures to lab personnel and to avoid damage to lab equipment via corrosion

**Pipette Technique**

Note: The technique below can also be utilized with a mechanical or electronic pipettor by substitution of the bulb/pipette combination with the pipettor.

**Procedure**

1. Uncap the reagent bottle and insert pipette with bulb that has been compressed.
2. Slowly decompress the bulb to draw slightly more than the desired amount into the pipette.
3. Now manipulate the bulb (compressing and decompressing) until the desired level of hydrofluoric acid has been obtained.

**OR**

If an analytical pipette is being utilized, remove the bulb and quickly stopper the bulb end of the pipette. Manipulate the bulb end opening with a finger/thumb, allowing excess liquid to drain out of the pipette until the desired liquid level is obtained.

1. Transfer the pipette of hydrofluoric acid to the intended vessel and expel the hydrofluoric acid from the pipette. Be careful not to drip as you transfer.
2. Close the reagent bottle and place it back into its proper storage location.
3. Clean equipment and the work surface in the appropriate manner.



**Figure 3**. Liquid transfer via pipette. Note that glass should NOT be used with hydrofluoric acid; use polyethylene or polypropylene lab ware.

**Graduated Cylinder Technique**

**Procedure**

1. Place a graduated cylinder on a level and stable surface.
2. Remove the cap from reagent bottle and place a funnel in the mouth of the graduated cylinder.
3. With the lip of the reagent bottle in direct contact with the funnel, pour the hydrofluoric acid into the graduated cylinder until the liquid reaches the desired level. You may need to use a Pasteur pipette to get the exact desired level of hydrofluoric acid.
4. Once the desired amount of hydrofluoric acid is obtained in the graduated cylinder and with the lip of the graduated cylinder in direct contact with the funnel of your vessel, slowly pour the graduated cylinder contents into the receiving vessel.
5. Close the reagent bottle and return to its proper storage location.
6. Clean the equipment and the work surface in the appropriate manner.

**NOTE:** When diluting hydrofluoric acid with water, always add the HF to the water, never vice-versa. Concentrated acids tend to have a greater density and don’t allow added water to mix well. This causes exothermic hot spots and can cause the acid to splatter. Slowly adding the acid to water alleviates this effect.



**Figure 4.**  Liquid transfer via graduated cylinder. Note that glass should NOT be used with hydrofluoric acid; use polyethylene or polypropylene lab ware

## Waste disposal procedure.

If necessary, consult the [Campus waste disposal guide](https://www.drs.illinois.edu/site-documents/WasteDisposalGuide.pdf) and [chemical waste quick start guide.](https://www.drs.illinois.edu/Waste/ChemicalWasteQuickStartGuide)

Upon completion of work with hydrofluoric acid, dispose of the waste material in the following manner:

* Store the waste in an appropriate container. Container must have the description of the contents *and* the appropriate hazard warnings. For example: “48% Hydrofluoric acid” and the warnings “Toxic” and “Corrosive”.
* Each waste stream must have a unique number (UI#) assigned by DRS to identify a chemical waste generated on campus. Label the container clearly with a description of the contents and the corresponding UI#. Some UI#’s for chemicals containing hydrofluoric acid are listed below.
  + # 15292 – Hydrofluoric acid
  + #573 – Hydrofluoric acid (unused)
  + #10621 – Hydrogen fluoride pyridine complex
  + #14737 – Buffered oxide etch
* Notify the DRS Chemical Waste Section by sending a completed CWM-TRK form to [this email](mailto:cws@illinois.edu).

# Record of changes made to this SOP

Describe the changes made to this document since its creation.

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| **Date of change** | **Changed by** | **Description of change** |
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Standard Operating Procedure for

# Training record

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