UNIVERSITY OF VICTORIA
Occupational Health, Safety and Environment

Chemical Safety – Special Hazards

Safe Work Procedure (SWP – 010)

Hydrofluoric Acid

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REVISION HISTORY

	Revision Date	*Author*	*Position*
1.	03-April-2019	Troy Hasanen	OHSE Consultant
2.	30-Nov-2022	Paraskevi Lagaditis	OHSE Consultant
3.	06-Jan-2025	Paraskevi Lagaditis	OHSE Consultant

DOCUMENT APPROVAL

Approved by: Laboratory Safety Committee

Jody Spence — December 6, 2022

Chair, Laboratory Safety Committee — *Date Approved*

**This revision replaces all previous versions of this document. If a copy is printed, it is the users' responsibility to verify the copy is the most current version of the document.*

University of Victoria

PURPOSE

To provide guidance and instruction of the safe use of hydrofluoric acid (HF) as well as hydrogen fluoride (HF) generating chemicals in laboratories. In addition to this general Safe Work Procedure (SWP), each lab must develop a lab-specific work procedure unique to the experiments and activities being performed. The Lab SWP must be reviewed by OHSE (see Procedures, #7)

SCOPE

The SWP applies to handling, storage and disposal of hydrofluoric acid used in laboratories. Consideration for fluorine containing chemicals that produce hydrofluoric acid as a by-product is also included.

TRAINING

The following training is required to be completed prior to being permitted to prepare and work with hydrofluoric acid:

- WHMIS
- Lab Safety for Lab Workers
- Lab SWP with documented signoff by the individual and their supervisor.

Refresher training in the General and Lab SWP must be provided when:

- there has been an extended timeframe of inactivity, or
- there has been an incident or injury, or
- 2 years has elapsed since the original training

REGULATION AND POLICY

The University of Victoria will follow WorkSafeBC Occupational Health and Safety Regulation Part 30, and the University of Victoria Occupational Health, Safety & Environment Department.

RESPONSIBILITY

It is the responsibility of personnel undertaking activities with special hazards to complete all required training and adhere to these safe work procedures, including any additional lab or job-specific procedures.

It is the PI's or supervisor's responsibility to ensure that individuals working with special hazards have been trained prior to commencing work and have demonstrated competency in safely performing all duties associated with the special hazard in accordance with these procedures.

MATERIALS

Spill X-A or calcium hydroxide ($Ca(OH)_2$) solution or magnesium hydroxide ($Mg(OH)_2$) solution are commonly used as HF neutralizers. Spill X-A is a proprietary product comprised of magnesium oxide (60-100%) blended with other chemical additives. Either of the three HF neutralizers produce calcium fluoride (CaF_2) or magnesium fluoride (MgF_2).

AVOID sodium or potassium carbonate (Na_2CO_3 or K_2CO_3) and sodium or potassium hydroxide (NaOH or KOH) to neutralize spills because sodium or potassium bifluoride are produced as intermediates. These intermediates are HF generating chemicals and will release gaseous HF when exposed to heat.

Sodium carbonate (Na_2CO_3) of around 10% concentration is commonly used as a mild decontamination solution of surfaces and reusable labware or gloves within a fume hood. Calcium chloride ($CaCl_2$) can be used to decontaminate; calcium chloride will bind to fluoride anion (to produce calcium fluoride, CaF_2) and the resulting solution will contain corrosive hydrochloric acid (HCl). However, since the solution will be acidic there is no quick method to ensure all the HF is neutralized in the decontamination process.

Use chemically compatible containers (e.g. polyethylene or Teflon) and do not use glass to store or transfer HF.

When using HF, you must wear the following protective equipment and follow these safety precautions:

- Laboratory coat and chemically resistant apron. Ensure closed toed shoes are worn and no exposed skin when handling hydrofluoric acid or other corrosive materials.
- Always use goggles together with a face shield when handling concentrated hydrofluoric acid to ensure no exposed skin and adequate eye protection is provided.
- Gloves shall be worn at all times when handling hydrofluoric acid.
    - Medium or heavyweight viton, nitrile, neoprene or butyl can be worn. Nitrile gloves are not recommended for handling $\geq$ 30% hydrofluoric acid
    - Use gloves that cover the hands, wrists and forearms
    - A second pair of nitrile exam gloves should be worn under the gloves to protect against leaks.
    - Inspect gloves prior to use. If gloves become contaminated with HF, remove them immediately, thoroughly wash hand, and check your hands for any sign of contamination.
    - Contaminated reusable gloves (medium or heavyweight viton, nitrile, neoprene or butyl gloves) must be decontaminated after working with HF (see Decontamination steps below)
    - Contaminated disposable (e.g. nitrile gloves) gloves should be decontaminated before disposal with HF contaminated solid waste.
- An emergency eyewash/shower is required within 5 seconds walking distance of the work area but no further than 6 meters (20 feet).
- In case of skin exposure, the topical antidote calcium gluconate gel (Calgonate) must be within reach of the lab worker before commencing work with HF. Disposable nitrile exam gloves shall also be available to apply the calcium gluconate gel. Ensure the gel is not expired and replace after the expiration date has passed as well as if Calgonate gel was applied in an exposure incident.
- In case of HF ingestion, Milk of Magnesia is an antacid with magnesium hydroxide as the active ingredient that can be taken orally.

HAZARD

Hydrofluoric acid (HF) is a corrosive acid used for many processes including mineral digestion, surface cleaning, glass etching, and biological staining. HF is a clear and colorless liquid with an irritating odor at low concentrations. HF is a very hazardous, necrotizing acid since it can quickly penetrate tissues causing deep tissue damage, systemic toxicity and decalcify bone. Dermal burns from HF may not be noticed or

produce pain until 1 up to 24 hours after exposure. Even very low HF concentrations (e.g. 1 or 2%) may cause delayed symptoms and must be treated immediately. Prevention of exposure or injury must be the primary goal when working with HF.

Many chemicals containing fluorine may react with acid or water to produce HF. Review the SDS of all fluoride compounds and ensure the appropriate safety precautions are followed to reduce the risk of creating a HF hazard.

Common hydrofluoric acid (HF) generating chemicals

• Boron trifluoride diethyl etherate ($BF_3 \cdot OEt_2$)	• Tetrabutylammonium fluoride (TBAF)	• Silver tetrafluoroborate ($AgBF_4$)
• Tetrafluoroboric acid (HBF_4)	• Sodium fluoride (NaF)	• Silver hexafluorophosphate ($AgPF_6$)
• Hexfluorophosphoric acid (HPF_6)	• Potassium fluoride (KF)	• Silver hexafluoroantimonate ($AgSbF_6$)
• Phenylmethylsulfonyl fluoride	• Ammonium fluoride (NH_4F)	• Stannous fluoride (SnF_2) or Tin fluoride (SnF_4)
• Tetraethylammonium fluoride	• Cesium Fluoride (CsF)	• Xenon difluoride (XeF_2) or Xenon tetrafluoride (XeF_4)
• Pyridinium fluoride (Py-HF)	• Potassium bifluoride (KHF_2)	• Ammonium bifluoride ($(NH_4)HF_2$)

PROCEDURE

1. Handling

a. Never work alone or after hours with HF.

b. Don personal protective equipment as outlined under Materials.

c. Conduct all work with HF inside a chemical fume hood to minimize inhalation of vapors.

d. Post a sign on the fume hood “Danger Hydrofluoric acid HF is in use”.

e. Post HF emergency procedures and print a copy of the SDS in the work area.

f. Ensure the HF specific spill kit is easily accessible

g. Ensure calcium gluconate gel topical antidote is not expired and within reach.

h. Ensure HF neutralizers are easily accessible in the fume hood

i. Ensure the work surface is clean and free of clutter to avoid and safely manage any spills.

j. Use secondary containment bins to transport HF to the work area

k. Use secondary containment tray to conduct work within

l. Keep containers capped until actual use

m. Only use chemically compatible containers and labware to handle HF (such as polyethylene or Teflon)

n. Limit the quantity of HF feasible for the specific task

o. Consider purchasing diluted HF if available to avoid diluting concentrated HF solutions

2. Storage

a. Avoid storing excessive volumes of HF

b. Do not store more than 1 L of concentrated (40-50%) HF. Higher quantities will require a specific risk assessment and approval.

c. Use chemically compatible containers (such as polyethylene or Teflon) with a sealed lid.

d. Never store HF in glass, metal or ceramic containers

e. Ensure HF is stored away from incompatible chemicals such as ammonia or other alkaline materials

f. Use a secondary container to store HF in corrosive cabinets

3. Spills

a. **DO NOT USE** Organic spill kits that contain Floor-dri, kitty litter, sand or the grey spill pads because HF reacts with silica to produce silicon tetrafluoride (SiF_4), a toxic gas. Hydrofluoric acid spill kits are available through OHSE

b. To ensure medical personal are aware of the hazards and treatment of any HF exposure, bring a copy of the SDS sheet and this SWP as a further reference

c. Follow OHSE's general spill response instructions.

d. Do not attempt to clean up any spill if not trained. Seek assistance or call Campus Security (250-721-7599)

e. Specific steps for small spills of HF within the secondary containment working area:

i. Get assistance and notify your supervisor. Never rush in or work alone

ii. Clearly assess the situation before starting clean up and use proper protective equipment

iii. Use either

a) Calcium hydroxide, magnesium hydroxide or Spill X-A to neutralize. **DO NOT USE** sodium or potassium carbonate **NOR** sodium or potassium hydroxide to neutralize.

b) A spill absorbent specified for HF should be used for clean-up**. DO NOT USE THE GREY SPILL PADS FOR HF CLEAN UP**

iv. Add neutralizers slowly as the reaction can be vigorous from outside of the spill inwards. Cover the entire area completely. Heat will vaporize HF and increase risk exposure

v. Wait for 30 minutes

vi. Test with pH paper until the spilled material is within the neutral range of pH 6-8

vii. Scoop the absorbed neutralized material into an appropriately sized plastic container.

viii. Wipe up any residue with a moist paper towel or rag

ix. Soak the area with detergent, then rinse with water

x. Collect and label all materials used in the clean-up for disposal through the hazardous waste system indicating the material is “Neutralized hydrofluoric acid HF spill absorbent and debris”

f. Specific steps for any spill of HF outside of the containment area or outside of the fume hood:

i. Secure the area and alert others

ii. Immediately evacuate the area

iii. Post “do not enter” signs on the doors of the lab

iv. Contact Campus Security at 250-721-7599

g. Complete a Department Incident & Investigation Report form to document and review the spill incident.

4. Decontamination

a. Decontamination must be performed within a fume hood to contain rapid gas release

b. Rinse containers, lab ware and gloves with water three times and collect washings for hazardous waste disposal.

c. Rinse with 10% sodium carbonate solution and collect pre-rinse washing

i. Sodium fluoride (NaF) by-product is an HF generating species that is produced and washings must be handled as hazardous material

d. Test reusable labware and gloves with pH strips.

e. Pat dry with paper towel reusable containers, lab ware and gloves.

f. Clean fume hood and contaminated surfaces with 10% sodium carbonate solution

g. Soak the work surface area with detergent, then rinse with water

h. Double bag all disposable items and dispose as HF contaminated solid waste.

i. Any clothes contaminated with HF must be disposed via hazardous waste.

5. First Aid and Emergencies

a. Call 911 to summon an ambulance if there is a medical emergency.

b. Call Campus Security at 250-721-7599 for first aid.

c. To ensure medical personal are aware of the hazards and treatment of any HF exposure, bring a copy of the SDS sheet and this SWP as a further reference

d. Immediately start the first aid treatment to prevent burns and serious injury.

e. Often symptoms of HF exposure are delayed. Any skin, eye, or tissue contact with HF should receive immediate first aid and medical treatment, even if the injury appears minor and no pain is felt.

f. Consider taking home the calcium gluconate gel (Calgonate) the day you used HF (or HF generating compound) in case of late indication of exposure

g. In cases of suspected exposure noticed on campus, Campus Security should call an ambulance. Do not drive nor take public transportation due to potential heart arrhythmia

h. In cases of suspected exposure noticed off-campus, the individual should call an ambulance. Do not drive nor take public transportation due to potential heart arrhythmia

i. Skin Contact:

    i. Immediately proceed to the nearest emergency shower and rinse the affected area thoroughly with water for maximum of 5 minutes to not delay application of calcium gluconate.

    ii. While the victim is being rinsed with water, ensure 911 and Campus Security (250-721-7599) has been called for medical assistance.

    iii. Remove all contaminated clothing while continuing to flush the area with water.

    iv. Massage calcium gluconate gel (Calgonate) into the affected area. Be sure to wear nitrile gloves (double glove is best) while applying to prevent possible secondary HF burns. Apply the gel frequently and massage continuously until pain and/or redness disappears or emergency medical assistance arrives. (note calcium fluoride will precipitate when the gel is applied and the gel will turn white)

    v. Continue applying calcium gluconate gel (Calgonate) to the affected area while transporting to the hospital.

j. Eye Contact:

    i. Do not apply calcium gluconate gel to eyes.

    ii. Immediately proceed to the nearest eyewash station and flush eyes with water for at least 15 minutes. Ensure eyelids are open for thorough flushing.

    iii. While the victim is flushing eyes with water, ensure 911 and Campus Security has been called for medical assistance.

    iv. Continue washing the affected area until emergency medical assistance arrives.

g. Ingestion:

    i. Do not induce vomiting.

    ii. Drink large quantities of milk, water, or milk of magnesia.

h. Inhalation:

    i. Immediately move to an area with fresh air.

6. Waste Disposal

a. HF liquid waste should be separately collected in a chemically compatible container with a sealed lid. Do not mix with other acidic waste.

b. Collect all contaminated solid materials for disposal into a chemical compatible container or a Ziploc bag (such as disposable gloves, spill pads, paper towels etc).

c. Double bag all HF (solid or liquid) waste containers and Ziploc bags.

d. Clearly label all waste containers as “Hydrofluoric acid HF waste”

e. Stick a green hazardous waste sticker on all double bagged HF waste

f. Complete the hazardous waste disposal form to request a pick-up of any hazardous waste

7. Lab SWP

In additional to this general SWP, each lab that using HF or using a chemical that generates hydrofluoric acid as a by-product requires a Lab SWP that includes specific procedures for:

a. Maximum permitted volume and concentration of HF or hydrofluoric acid generating reactant used.
b. Storage details.
c. Designated areas to conduct experiments and signage.
d. Experiment details including specifics of labware required.
e. Spill containment and response.
f. Emergency first aid response.

REFERENCES

1. University of Pittsburgh, *Guidelines for the Safe Use of Hydrofluoric Acid*, March 2010.
2. Harvard University, *Guidelines for the Safe Use of Hydrofluoric Acid*, March 2007.
3. Honeywell, *Recommended Medical Treatment for Hydrofluoric Acid Exposure*, 2010.
4. Concordia University, *Hydrofluoric Acid Safety Guidelines*, n.d.
5. University of Washington *Hydrofluoric Acid SOP*, 2017.
6. University of British Columbia *Working Safely with Hydrofluoric Acid,* 2017.