Hydrofluoric Acid and Related Fluoride-Containing Mixtures Standard Operating Procedure

Revision: December 20, 2023

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Laboratory Director (LD) Approval is Required Prior to Performing this Procedure

This standard operating procedure (SOP) outlines the handling and use of hydrofluoric acid and related fluoride-containing mixtures. Review this document and supply the information required in order to make it specific to your laboratory. In accordance with this document, laboratories should use appropriate controls, personal protective equipment, and disposal techniques. All laboratory workers must read and understand the Laboratory Emergencies SOP prior to commencing any work in a laboratory. In addition, all workers must be familiar with the unique emergency and first aid requirements specific to hydrofluoric acid described in this document.

Description [Provide additional information as it pertains to your research protocol]

Hydrogen fluoride is a colorless, corrosive gas or liquid that is made up of one hydrogen and one fluorine atom. It has a boiling point of 19.5 °C, fumes strongly, readily dissolves in water, and both the liquid and vapor will cause severe burns upon contact. The dissolved form is called **hydrofluoric acid (HF)**. **HF** is used in various applications, such as the fabrication of electronic components, glass etching, biological staining, and mineral digestion, to name a few.

HF poses particularly dangerous health hazards. HF is a strongly corrosive chemical. It readily penetrates the skin and mucous membranes, and can cause deep tissue destruction. Severity and timing of effects depends on the concentration, duration of exposure, and penetrability of the exposed tissue. Symptoms may start immediately or pain may be delayed. Life threatening systemic toxicity may follow dermal exposure with minimal external tissue damage; a seemingly minor exposure can lead to severe medical consequences.

Any confirmed or suspected exposure to HF must receive immediate first aid as described in this document, followed by immediate medical treatment from a physician.

In addition, some fluoride-containing mixtures* can release HF under certain conditions. An exposure to a mixture containing the following should receive the same first aid procedures as an HF exposure:

- Sodium fluoride (NaF) – may release HF in contact with strong acids.
- Potassium bifluoride (KHF_2) – reacts with water to produce HF.
- Ammonium fluoride (NH_4F) – reacts with water to produce HF.
- Ammonium bi-fluoride (NH_4F_2) – produces HF when dissolved in water or heated above 240 °C.
- Sulfur tetrafluoride (SF_4) – reacts with water and strong acids to produce HF.

** This list is not all-inclusive and other related fluoride-containing compounds may release HF depending on the amount, concentration and pH at which they are used. Always ask a supervisor, or contact EHS, if you are unsure about the potential hazards of a mixture.*

Process [Write the steps for using the chemical in your research protocol]

Potential Hazards [Provide additional information as it pertains to your research protocol]

- HF can penetrate skin, deep into the tissue layers. Once absorbed, HF dissociates into H^+ and F^- ions. The free fluoride ion will bind primarily with calcium but can also bind with magnesium, sodium and potassium to disrupt cellular functioning.
- Concentrated HF (greater than 50% w/w) produces extremely painful, deep tissue burns. Concentrated HF exposure covering as little as 2% of the body can be fatal.
- Lower concentrations of HF (20% to 50% w/w) may not produce symptoms for up to eight hours.
- With concentrations of less than 20% w/w, the latency period may be up to twenty-four hours. Thus, it is critical to seek medical attention after any exposure, even if there is no pain.
- Fluoride-containing mixtures may react with strong acids or water to produce HF. If the manner in which the mixture is used can create HF in the above listed concentrations, follow the precautions for HF.
- Calcium gluconate gel will bind to the fluoride ions and prevent further tissue destruction, but it must be applied immediately after exposure (even if there is no pain) to be effective.

Occupational Exposure Limits (OELs):

- The Occupational Safety and Health Administration (OSHA) has established a permissible exposure limit (PEL) of 3 ppm averaged over an eight-hour work shift for HF.
- OSHA has established a PEL of 2.5 mg/m^3 averaged over an eight-hour work shift for NaF, KHF_2, NH_4F, and NH_4F_2 (measured as Fluorine).
- MIOSHA has not established a PEL for SF_4, however The National Institute for Occupational Safety & Health (NIOSH) has established a Ceiling Recommended Exposure Limit (REL-C) of 0.1 ppm that should not be exceeded at any time.

Contact EHS for assistance in performing an exposure assessment.

Engineering Controls [Provide additional information as it pertains to your research protocol]

- First and foremost, consider alternate methods and use a less dangerous acid if possible.
- Always work with HF in a chemical fume hood or locally exhausted enclosure (i.e. a wet bench).
- Provide exhaust ventilation or other engineering controls to keep the airborne concentrations of vapors below their respective threshold limit value.

Work Practice Controls [Provide additional information as it pertains to your research protocol]

- Always consult the Safety Data Sheet (SDS) for your specific product prior to beginning work.
- Lab personnel should work in the buddy system and no one should work alone with HF. Only persons who have read and understood this SOP and who are suitably trained should use HF.

- Designate areas where HF is stored and manipulated.
- Purchase HF in the smallest amounts possible.
- Stock calcium gluconate gel (Calgonate or equivalent) to be used as first aid in case of an HF exposure. Prior to using HF, make sure the calcium gluconate tube is unopened and unexpired.
- Do not heat HF.
- Perform a dry run to identify and correct potential hazards.
- Add acid to water, not water to acid.
- Line work surfaces with plastic-backed absorbent paper and/or a containment tray of compatible material.

Personal Protective Equipment **[Provide additional information as it pertains to your research protocol]**

Wear a fully-buttoned lab coat with sleeves extended to wrists, face shield AND safety goggles, elbow length neoprene outer gloves and nitrile inner gloves, long pants (or other clothing covering the entire leg), rubber apron, and closed toe shoes. For brief use of small amounts of dilute HF (<50 ml), double nitrile gloves can be used but must be changed immediately if splashed or thought to be contaminated. Nitrile gloves are not recommended for handling ≥ 30% w/w solutions of HF.

Transportation and Storage **[Provide additional information as it pertains to your research protocol]**

- Transport in secondary containment, preferably a polyethylene or other non-reactive acid/solvent bottle carrier.
- Store:
    - Only in a tightly closed container made from polyethylene, fluorocarbon, or lead.
    - HF dissolves glass, ceramics, and some metals and must never be stored in containers made from these materials.
    - In a compatible secondary container to capture leaks or spills.
    - With other inorganic acids, away from bases and other incompatibles including glass, concrete, water, oxidizers, alkalis, combustibles, organics ceramics, and metal (unless the metal has a corrosion-proof coating).
    - In a cool, well-ventilated area.
    - Below eye level.
- Do not store under the sink or on the floor.

Waste Disposal **[Provide additional information as it pertains to your research protocol]**

Handle and store HF wastes following the guidelines above while accumulating wastes and awaiting chemical waste pickup. Because most spent, unused and expired chemicals/materials are considered hazardous wastes, they must be properly disposed of. ***Do not dispose of chemical wastes by dumping them down a sink, flushing in a toilet or discarding in regular trash containers, unless authorized by EHS Hazardous Materials Management (HMM).*** Contact EHS-HMM at (734) 763-4568 for waste containers, labels, manifests, waste collection and for any questions regarding proper waste disposal. Also refer to the EHS Hazardous Waste webpage for more information.

Exposures/Unintended Contact [Provide additional information as it pertains to your research protocol]

 ***If the employee is in need of emergency medical attention, call 911 immediately*** 

Any confirmed or suspected exposure to HF must receive immediate first aid, followed by immediate medical treatment from a physician.

When seeking medical care for HF exposures, provide the following information to the EMS team, and/or physician:

- A copy of the SDS
- The concentration of HF
- Time of exposure, duration of exposure, and how exposure occurred
- Body parts affected or exposed, and the percent of body surface area affected
- Summary of first aid measure given, including when calcium gluconate gel was first applied, the body areas to which the treatment was applied, and how many times the treatment was applied in total

In case of skin exposure:

- IMMEDIATELY shower or flush with plenty of water.
- Remove contaminated clothing from affected area while rinsing or in the shower.
- Double-bag contaminated clothes and shoes.
- Rinse with water for **5 minutes**.
- Immediately after rinsing, use a **gloved** hand to apply calcium gluconate gel to the skin and massage it in. Continue to apply with a gloved hand and take/send the calcium gluconate gel along with the victim when seeking medical attention.

In case of eye exposure:

- Flush eyes with water for **15 minutes**.
- Hold the eyelids open and away from the eye to allow thorough flushing.
- Seek medical treatment as indicated below.
- Ice water compresses may be applied to eyes while transporting the person to the doctor.

For situations with risk of inhalation exposure:

- Remove all persons from the contaminated area.
- Prevent others from entering.
- Contact the University of Michigan Division of Public Safety and Security (DPSS) at 911 to request assistance.

NOTE: If an ambulance is needed, call the University of Michigan Division of Public Safety and Security (DPSS) at 911 to request assistance.

Report all work related accidents, injuries, illnesses or exposures to Work Connections within 24 hours by completing and submitting the Illness and Injury Report Form.

Follow the directions on the Work Connections website Where to go for treatment to obtain proper medical treatment and follow-up.

Complete the Incident and Near-Miss Report form.

Treatment Facilities

U-M Occupational Health Services -- Campus Employees
Mon-Fri 7:00 am - 4:30 pm
After hours - go to U-M Hospital Emergency Dept. -- Urgent Care Clinic
380 Med Inn building
1500 East Medical Center Drive, Ann Arbor (734) 764-8021

University Health & Counseling -- University students (non-life threatening conditions)
To view the hours of operation, please visit the University Health & Counseling website.
207 Fletcher Street, Ann Arbor (734) 764 - 8320

UMHS Emergency Department -- after clinic hours or on weekends
1500 East Medical Center Drive, Ann Arbor (734) 936-6666

Spill Procedure **[Provide additional information as it pertains to your research protocol]**

- **A commercial spill kit (i.e. Spill 911 Inc. "HF Acid Eater" or Calgonate "HF Spill Neutralizer") that is specific for HF must be stocked in the lab. Fisher Scientific and Grainger are two companies available through M-Marketsite that carry spill kits specific for HF.**
    - Do NOT use organic spill kits that contain Floor-Dri, kitty litter, or sand because HF reacts with silica to produce silicon tetrafluoride (a toxic gas).
- When a spill occurs, **personal safety should always come first.**
- Alert and clear everyone in the immediate area where the spill occurred.
- On the U-M campus, any spill of HF outside of a fume hood must be referred to EHS-HMM by calling the University of Michigan Division of Public Safety and Security (DPSS) at 911.
- Small spills of HF in the fume hood (<100 mL) can be absorbed using a spill absorbent specified for HF. After the spill has been completely absorbed, wipe down spill site with water. All materials used to clean the spill should be placed into a plastic bucket and sealed with a lid. Label the container with a hazardous waste label and contact EHS-HMM at (734) 763-4568 to request a pick up.
- **For spills of HF greater than 100 mL in a fume hood or any amount outside of a fume hood, leave the lab and call University of Michigan Division of Public Safety and Security (DPSS) at 911 to request assistance from EHS**. Do not take any action to cover the spill. Post a warning on the lab and do not allow others to enter. Have a person available that has knowledge of the incident and laboratory to assist emergency personnel.

For additional information regarding spill response procedures, refer to the EHS Hazardous Waste Spill Response Web page.

Emergency Reporting

Report all emergencies, suspicious activity, injuries, spills, and fires to the University of Michigan Police (DPSS) by calling 911 or texting 377911. Register with the University of Michigan Emergency Alert System via Wolverine Access.

Training of Personnel

All personnel are required to complete the ***General Laboratory Safety Training*** (**BLS025w** *or equivalent*) and ***Hydrofluoric Acid and Ammonium Fluoride Safety in the Laboratory Training*** (**BLS026w**) via the EHS My LINC Web page. Furthermore, all personnel shall read and fully adhere to this SOP when handling HF.

References

- Honeywell. (2018, June). *Recommended Treatment for Hydrofluoric Acid Exposure*
- National Research Council (2011). *Prudent Practices in the Laboratory: Handling and Management of Chemical Hazards.*

Certification

I have read and understand the above SOP. I have received approval from my Lab Director to perform this procedure. I agree to contact my Lab Director if I plan to modify this procedure.

Name	Signature	UMID #	Date

Laboratory Director **Revision Date**

Revision History (Do not print as part of the SOP)		
12/20/2023	Partial Revision	Added OELs section and updated training section. (BR)
11/21/2022	Partial Revision	Revised and expanded to include references to related fluoride-containing compounds. (BR)
05/03/2022	Partial Revision	Reviewed and updated links, exposure protocols, emergency spill procedures, and training requirements. (LGS)
05/18/2020	Partial Revision	Updated editing rights to headings (RSH)
03/04/2019	Annual Revision	