**Hydrofluoric Acid (HF)**

**STANDARD OPERATING PROCEDURE (SOP)**

**Type of SOP:** ☐ Process/Equipment ☒ Hazardous Chemical ☐ Hazardous Class

**All personnel subject to these SOP requirements must review a completed SOP and sign the associated training record. Completed SOPs must be kept in the laboratory’s safety binder or be otherwise readily accessible to laboratory personnel. Electronic access is acceptable. SOPs must be reviewed, and revised where needed, as described in the** [**SJSU Chemical Hygiene Plan**](http://www.sjsu.edu/fdo/departments/ehs/lab/Chemical%20Hygiene%20Plan_20191017-final.pdf)**.**

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| Date SOP Written: | | **4/2/2020** | |  | Approval Date: | | | **4/3/2020** |
| SOP Prepared by: | | **Prof. Jane Doe** | | | | | | |
| SOP Reviewed and Approved by (name/signature): | | | | **Prof. Jane Doe** | | | | |
| Department: | | **Chemistry** | | | |
| Principal Investigator/ Laboratory Supervisor: | | **Prof. Jane Doe** | | | | Phone: | **408-924-XXXX** | | |
| Emergency Contact(s): | | **Prof. Jane Doe** | | | | Phone: | **(personal contact number/cell number)** | | |
|  | | **Randy Kirchner** | | | |  | **408-924-5004** | | |
|  | | **Prof. John Smith** | | | |  | **408-924-XXXX** | | |
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|  | |  | | | |  |  | | |
| Location(s) covered by SOP: | Building: | | **Duncan Hall** | | | Lab Phone: | **408-924-XXXX** | | |
| Room #(s): | | **435** | | |

1. **HAZARD OVERVIEW**

Hydrofluoric (HF) acid solutions are clear and colorless with a density similar to that of water. HF is extremely corrosive and can cause deep tissue damage and systemic toxicity. The most widely-known property of HF is its ability to dissolve glass and bone. Hydrofluoric acid also attacks glazes, enamels, pottery, concrete, rubber, leather, and many metals and organic compounds. Upon reaction with metals, explosive hydrogen gas may be formed.

1. **HAZARDOUS CHEMICAL(S)/CLASS OF HAZARDOUS CHEMICAL(S)**

Although HF is a weak acid (pKa = 3.17), exposures can be fatal or cause permanent bone, tissue, and nerve damage. HF is a highly corrosive liquid and a contact poison and should be handled with extreme care (i.e. beyond what is generally required to handle other mineral acids). HF is a lipid-soluble molecule that penetrates tissue more rapidly than typical mineral acids, due to its low dissociation constant. Concentrated HF has a boiling point of only 67 °F (19.4 °C). Because of the ability of HF to penetrate tissue, poisoning can occur readily through minimal exposure of skin or eyes, or when inhaled or ingested. HF irreversibly binds calcium which affects nerve signaling, delaying detection of exposure (burns may not initially be painful and may not be evident until sometime after exposure). This property may also lead to:

* Cardiac arrest from higher exposure levels to a small portion of your body (as little as 25 in2 of skin to concentrated acid); and
* Dissolution of calcium from bone from lower exposure levels if left untreated.

HF is classified under the GHS system with the following Hazard Codes for toxicity and corrosivity:

* **H300** (Fatal if swallowed);
* **H310** (Fatal in contact with skin);
* **H330** (Fatal if inhaled);
* **H314** (Causes severe skin burns and eye damage); and
* **H318** (Causes serious eye damage).

In short, HF poses a serious threat to the health and safety of laboratory personnel, emergency responders and waste handlers. Additional information and data for HF is available from [PubChem](https://pubchem.ncbi.nlm.nih.gov/compound/14917#datasheet=lcss&section=Top) and [Honeywell](#Honeywell).

1. **ENGINEERING/VENTILATION CONTROLS**

The following is a general plan for work with Hydrofluoric Acid:

1. All open work with HF concentrations greater than 1% shall be done in a certified, properly-functioning chemical fume hood or similar exhaust hood;
2. For processes where HF vapor may be produced, the fume hood should have a PVC liner and a non-glass sash (e.g. Lexan); and
3. Using HF at elevated temperatures requires facility-specific engineering/ventilation controls. Contact the Chemical Hygiene Officer or [alexi.ball-jones@sjsu.edu](mailto:alexi.ball-jones@sjsu.edu?subject=Using%20HF%20at%20elevated%20temperatures) for assistance.
4. **ADMINISTRATIVE CONTROLS**

The following elements are required:

1. Complete laboratory safety training prior to working in the laboratory;
2. Complete laboratory-specific safety orientation and training on laboratory-specific safety equipment, procedures, and techniques to be used, including the location of laboratory safety equipment (emergency eyewash, safety shower, fire extinguisher);
3. Demonstrate competency to perform the procedures described in this SOP to the Principal Investigator (PI) or trainer;
4. Be familiar with the location and content of any Safety Data Sheets (SDSs) for the chemicals used (online SDSs are available from [MSDS online](https://msdsmanagement.msdsonline.com/8511b604-100d-449a-9a6b-366eff19da04/ebinder/?nas=True));
5. Inspect all equipment and experimental setups prior to use;
6. Follow best practices for the movement, handling, and storage of hazardous chemicals (see Chapters 5 and 6 of [Prudent Practices in the Laboratory](http://ucanr.edu/sites/ucehs/files/133892.pdf) for more detail). An appropriate spill cleanup kit must be located in the laboratory. Chemical and hazardous waste storage must follow an appropriate segregation scheme and include appropriate labeling. Hazardous chemical waste must be properly labelled, stored in closed containers, in secondary containment, and in a designated location;
7. Do not deviate from the instructions described in this SOP without prior discussion and approval from the PI; and
8. Notify the PI of any accidents, incidents, near-misses, or unexpected outcomes involving HF use described in this SOP.

**For HF, the following are also required:**

1. Never work alone. All work involving HF must be performed in the presence of at least one safety buddy. The safety buddy must be a person who has been trained in the use of HF and who is proficient with the HF emergency protocols set forth in this SOP. Furthermore, the safety buddy must be within audible and visible range of the person that is handling HF at all times, and must not be concurrently working with HF or any other compound or process that cannot be easily and safely abandoned;
2. HF must only be used in a room with a properly functioning eye wash. A safety shower must be available within 10 seconds of travel;
3. A supply of calcium gluconate (in solution or gel) **must** be within reach of the user. In addition, a recommended best practice is that a responder (e.g. a person trained on this SOP) should be within audible and visible range with easy access to calcium gluconate solution or gel to assist in the event of user exposure. The responder **must** wear nitrile or neoprene gloves when administering first aid to avoid secondary contamination;
4. The date the calcium gluconate solution or gel was received should be noted and the expiration date shall be monitored; calcium gluconate expires in 36 months;
5. If a reaction is left unattended, warning signs must be posted on the fume hood with the sash closed (or at the location where the unattended operation is occurring);
6. Never exceed the laboratory maximum quantity limit without prior approval from the PI/Laboratory Supervisor;
7. Use and store HF in polyethylene or PTFE containers. Glass, metal, or ceramic containers are not compatible with HF. All reactions involving HF should be carried out in plastic containers and transferred using disposable plastic Pasteur pipettes or a PTFE cannula;
8. Use a bottle carrier or other high-walled secondary containment when transporting HF between work areas; and
9. HF containers shall be stored as follows:
   1. Within a tightly-closed plastic (*e.g.*, polypropylene) secondary container segregated from other flammables and reactives as much as possible; and
   2. Segregated from oxides, organic chemicals, bases, or metals.

**REQUIRED:** Insert the laboratory-specific quantity limit for HF use, both amount and concentration. Use above this amount requires prior approval from the PI.

1. *In the Jane Doe lab, HF-pyridine is stored in the flammable materials freezer in room 435 in a secondary container made of polypropylene.*
2. *HF-pyridine secondary container shall NEVER be opened outside of the chemical fume hood.*
3. *Never use more than 14 mL of 70% HF-pyradine in any one reaction. Any use above this quantity must have approval by Prof. Doe.*
4. *All HF reactions shall be carried out at -40 C (dry ice/acetonitrile bath).*
5. **PERSONAL PROTECTIVE EQUIPMENT (PPE)**

At a minimum, long pants (covered legs) and closed toe/closed heel shoes (covered feet) are required to enter a laboratory or technical area where hazardous chemicals are used or stored.

In addition to the minimum PPE required upon entering a laboratory, the following are required for work with HF:

1. **Eye Protection** (must be ANSI Z87.1-compliant)**:**
   1. At a minimum safety glasses are necessary.
   2. Splash goggles may be substituted for safety glasses, and are required for processes where splashes are foreseeable or when generating aerosols.
   3. Ordinary prescription glasses are not acceptable eye protection and cannot be used in lieu of proper safety eyewear.
   4. Whenever possible, the fume hood sash shall be positioned to provide an additional barrier of protection. If this is not possible, a face shield should be considered when activities involve a potential splash.
2. **Body Protection**: At a minimum a chemically-compatible laboratory coat that fully extends to the wrist is necessary. A chemically-compatible lab coat may be substituted for other types of body protection (e.g. apron, disposable sleeves, etc.) so long as the substituted protection provides similar or better protection to the researcher.
   1. If a risk of fire exists, a flame-resistant laboratory coat that is NFPA 2112-compliant should be worn.
   2. For chemicals that are corrosive and/or toxic by skin contact/absorption additional protective clothing (e.g. face shield, chemically-resistant apron, disposable sleeves, etc.) are required where splashes or skin contact is foreseeable.
3. **Hand Protection**: Hand protection is needed for the activities described in this SOP. Define the type of glove to be used based on:
   1. The chemical(s) being used;
   2. The anticipated chemical contact (e.g. incidental, immersion, etc.);
   3. The manufacturers’ permeation/compatibility data; and
   4. Whether a combination of different gloves is needed for a specific procedural step/task.

Neoprene or nitrile rubber gloves are best for working with HF. When handling or using larger quantities of HF wear thick neoprene or nitrile rubber gloves with a disposable neoprene or nitrile glove worn under the outer glove. It is understood that using thick gloves can reduce dexterity, and may increase the possibility of spills, however they do provide superior protection when the risk of exposure is greater due to the quantity being used or handled. If wearing two layers of thinner neoprene or nitrile disposable gloves, change the outer pair frequently. Gloves should be changed following any contamination, and properly disposed as hazardous waste.

**REQUIRED:** Insert lab-specific descriptions of PPE and hygiene practices used with HF, including any specialized PPE needed for a procedural step or specific task.

***Eyewear:*** *Safety glasses are mandatory, safety goggles are optional but recommended. A face shield shall be worn for reactions involving greater than 2 mL of 70% HF-pyridine.*

***Gloves:*** *two layers of the thicker disposable purple nitrile gloves shall be used. The outer pair of gloves must be changed frequently and after every addition of HF. Always check outer gloves for any liquid after handling the reaction vessel, if gloves show any wetness, assume it could be HF and change both pairs of gloves.*

***Lab Coat/Body Protection:*** *A standard cotton or poly/cotton lab coat should be worn. Consider also wearing the acid-resistant reusable sleeves available for HF use. Sleeves must be worn for reaction scales over 10 mL 70% HF-pyridine.*

1. **SPILL AND EMERGENCY PROCEDURES**
2. **In case of skin contact with HF**:
3. Speed and thoroughness of washing off the acid is of primary importance. Move victim immediately under shower or other water source. Wash thoroughly with large amounts of running water. Remove clothing and continue to flush with water. If 2.5% calcium gluconate gel is available rinsing may be limited to 5 minutes, if gel is not available continue rinsing until medical treatment is rendered.
4. While the victim is being rinsed with water, have someone call to arrange medical treatment. If the exposure is to the eyes or covers a large area (> 25mL or whole hand or limb), **call 911** (or 408-924-2222 from a non-campus phone). For smaller exposures (e.g.; a few mL on the skin), seek medical treatment if the exposed individual wishes to do so. Report all exposures to the PI/Lab Supervisor and to EH&S calling (408) 924-1969 and via the [Employer’s Report of Occupational Illness or Injury](http://www.sjsu.edu/up/docs/risk/forms/wc_employers_report_5020.pdf) for employees or [Student and Visitor Accident Report](http://www.sjsu.edu/finance/docs/risk_forms_accident_stdvist.pdf) for students.
5. Immediately after thorough washing, start massaging 2.5% calcium gluconate gel into the burn site. Apply the gel frequently and massage continuously until pain/redness cease or professional medical care is available. The expiration date of calcium gluconate is 36 months. Responders **must** wear thick neoprene or nitrile gloves when applying the gel to prevent secondary HF burns to their hands.

**ALL HF BURNS SHOULD BE EVALUATED BY A PHYSICIAN EXPERIENCED IN MEDICAL TOXICOLOGY AND TREATMENT OF CHEMICAL BURNS**.

1. **In case of eye contact:**

Immediately flush eyes with water for at least 15 minutes under emergency eyewash or other water source. Contact lenses should be removed if possible. If only one eye is affected, be careful not to flush contaminated water into the other eye. If a sterile 1% calcium gluconate solution is available, washing may be limited to 5 minutes followed by irrigation of the eye with 1% calcium gluconate solution. Call 911 (or 408-924-2222 from a non-campus phone) and then EH&S at (408) 924-1969. If possible, provide continuous irrigation during transport.

1. **In case of inhalation**

Immediately move exposed individual to fresh air and get medical attention. Call 911 (or 408-924-2222 from a non-campus phone) and then EH&S at (408) 924-1969.

1. **If swallowed:**

DO NOT INDUCE VOMITING. Give large quantities of milk (preferable) or water. Never give anything by mouth to an unconscious person. In addition, exposed individual may be given several ounces of milk of magnesia, any calcium containing antacid, Maalox®, etc. or grind up and administer Tums™, Caltrate® or other antacid tablets with water. Call 911 (or 408-924-2222 from a non-campus phone) and then EH&S at (408) 924-1969 immediately.

**INGESTION OF HYDROFLUORIC ACID IS A LIFE-THREATENING EMERGENCY**.

1. **Spill Clean Up Guidelines**

Immediately assess amount spilled. Assess the extent of danger. Assist contaminated or injured persons. Evacuate the spill area. Notify the College Safety Team and EH&S (408-924-1969) to aid with spill clean-up.

* If a spill occurs outside of a fume hood, evacuate lab personnel to safe areas. Keep others from entering contaminated area (e.g., use caution tape, barriers, etc.).

If you have training, and chose to assist in the clean-up effort, the following are guidelines:

* Personal Protective equipment must be worn – natural rubber gloves (arm length), goggles, face shield, natural rubber apron/suit, long pants, closed-toe rubber/leather shoes, respirator approved for HF handling. Assure adequate personal protection with respirator if needed.
* Wear respiratory protection. Avoid breathing vapors, mist or gas. Do not attempt to clean up a spill outside of a fume hood or other general exhaust without respiratory protection, as HF vapor has extremely poor warning properties.
* If possible, confine the spill to a small area using a spill kit or absorbent material. Use neutralizing agent (sodium carbonate or a slurry of magnesium hydroxide) and liquid binding material (vermiculite, sand, kitty litter) to absorb spill.
* Pick up contaminated material with a disposable scoop and place in a double transparent plastic bag.
* Label and tag as hazardous waste and bring to hazardous waste pick up location. Keep in suitable, closed containers for disposal.

**REQUIRED:** Insert a description of the contents and location of HF-specific spill kit or spill clean-up materials. Additional details of lab-specific cleanup should be provided if applicable.

*HF-specific spill materials can be found by the entrance to the laboratory. Spill kit includes sodium carbonate for neutralizing HF spill and vermiculite for liquid binding. Spill kit also includes heavy-duty butyl rubber gloves for clean-up PPE.*

1. **WASTE MANAGEMENT AND DECONTAMINATION**

**Waste Management:**

Hazardous waste must be managed as outlined in [SJSU’s Chemical Hygiene Plan](http://www.sjsu.edu/fdo/departments/ehs/lab/Chemical%20Hygiene%20Plan_20191017-final.pdf), and must be [properly labeled](http://www.science.sjsu.edu/safety/HazWasteForm.pdf). In general, hazardous waste must be removed from your laboratory within nine months of the accumulation start date.

**REQUIRED:** Insert descriptions of laboratory-specific information on the waste streams generated, storage location, and any special handling/storage requirements.

*The workup of the reaction involves quenching the excess hydrofluoric acid with a solution of potassium or calcium carbonate. The aqueous washes should be put into a special, plastic aqueous waste container used for reactions involving hydrogen fluoride. The organic solvent removed under reduced pressure should be disposed of into an organic waste container. Solids contaminated with HF-pyridine (eg. disposable plastic pasteur pipettes and contaminated gloves) shall be disposed of in a plastic hazardous waste container for solid wastes.*

**Decontamination:**

A neutralizing agent specific to HF should be used for initial decontamination of surfaces. Any plastic ware used for an HF reaction should be decontaminated with an aqueous solution of calcium carbonate, then washed as normal. It is also recommended to wash the surrounding area in the fume hood with an aqueous solution of calcium carbonate.

**REQUIRED:** Insert description(s) of decontamination procedures for equipment, glassware, and/or controlled areas (e.g. gloveboxes, restricted access hoods, or designated portions of the laboratory).

*Any reusable plastic ware used for an HF-pyridine reaction should be decontaminated with an aqueous solution of calcium carbonate, then washed as normal with water followed by acetone. The fume hood work area shall be washed with an aqueous solution of calcium carbonate, then water after all other cleanup has been completed.*

Upon completion of work with HF and/or decontamination of equipment, remove gloves and wash hands with soap and water. Upon leaving the laboratory or designated HF work area, remove all PPE worn and wash hands and forearms as needed. Contaminated PPE should not be worn outside of the laboratory. Soiled lab coats should be sent for professional laundering. Grossly contaminated clothing/PPE, and disposable gloves must not be reused and should be disposed of as hazardous waste.

1. **DESIGNATED AREA**

**REQUIRED:** Insert description(s) of the designated area(s) for HF use and storage in your laboratory. The entire laboratory, a portion of the laboratory, a fume hood, etc. can be designated.

*Any fume hood in 435 can function as a designated area. Fume hoods should be clean and free of clutter during the reaction.*

1. **DETAILED PROTOCOL**

**REQUIRED:** Insert the lab-specific protocol for the process, hazardous chemical(s), or hazard class described in this SOP. Include any relevant resources such as journal articles, patents, etc. as desired.

*The following procedure describes the* ***ONLY*** *use of HF in the Jane Doe laboratory, a nucleophilic aromatic substitution used to replace an Ar-NH2, and giving rise to an Ar-F bond. The process involves the use of tert-butyl nitrite and pyridine and evolves nitrogen gas. This reaction should NEVER be tightly capped or the container could rupture from pressure build-up.*

*Briefly, tert-butyl nitrite and pyridine are highly flammable liquids and are potential carcinogens. Do not work near ignition sources while using tert-butyl nitrite and/or pyridine. For specific information on handling carcinogens, see the lab’s Carcinogen SOP.*

*To a plastic flacon tube equipped with a stir bar under inert atmosphere and charged with starting material (1 equiv) was added pyridine (0.6 M) and cooled to -40 ˚C. Subsequently a 1:3 diluted pyridine:HF-pyridine solution was made by cooling pyridine to -40 ˚C then adding HF-pyridine (roughly 80 equiv), dropwise using a disposable plastic pasteur pipette. The cooled, diluted HF-pyridine solution was then added via plastic pasteur pipette to the falcon tube containing starting material, very slowly and dropwise.* ***The dilution of HF-pyridine and the addition of the diluted solution to starting material shall be directly supervised by another lab member trained in HF first aid.*** *After 10 minutes, tert-butyl nitrite (2.5 equiv) was added to the reaction mixture. The reaction was then charged with argon and capped loosely to allow evolution of nitrogen gas (a reaction byproduct). After the reaction was complete by thin layer chromatography (7% methanol in dichloromethane) (generally done in about 2 to 3 hours) saturated CaCO3 was added slowly until the reaction reached pH 7. The reaction was stirred until the evolution of gas ceased (generally about 20 minutes), and the organic layer was collected and dried over NaSO4, concentrated in vacuo and the product was purified by column chromatography.*

*Aqueous, solid, and organic wastes are disposed of at the end of the reaction as described in Section 7.*

**TEMPLATE REVISION HISTORY**

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| --- | --- | --- | --- |
| **Version** | **Date Implemented** | **Author** | **Revision Notes:** |
| **1.0** | **4/3/2020** | **Alexi Ball-Jones** | **New template** |

**LAB-SPECIFIC REVISION HISTORY**

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| --- | --- | --- | --- |
| **Version** | **Date Approved** | **Author** | **Revision Notes:** |
| **1** | 4/3/2020 | **Dr. Jane Doe** | New template |
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**Documentation of Standard Operating Procedure Training**

*(Signature of all users is required)*

* Prior to using **Hydrofluoric Acid**, laboratory personnel must be trained on the hazards described in this SOP, how to protect themselves from these hazards, and emergency procedures.
* Ready access to this SOP and to a Safety Data Sheet for each hazardous material described in the SOP must be made available.
* The Principal Investigator (PI), or the Laboratory Supervisor if the activity does not involve a PI, must ensure that their laboratory personnel have attended appropriate laboratory safety training or refresher training within the last three years.
* Training must be repeated following any revision to the content of this SOP.

**Designated Trainer:** *(signature is required)*

I have read and acknowledge the contents, requirements, and responsibilities outlined in this SOP:

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| **Name** | **Signature** | **Trainer Initials** | **Date** |
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