STANDARD OPERATING PROCEDURE FOR HYDROFLUORIC ACID (HF) AND BUFFERED OXIDE ETCH (BOE)
GENERAL

Concentrated HF is considered "extremely" toxic (4 out of 4 on the health hazard scale). A plain, concentrated ammonium fluoride solution (NH$_4$F) is considered "very" toxic (3 on the health hazard scale) yet becomes "extremely" toxic when made more acidic, such as in BOE mixtures. For example, 20:1 BOE has much less HF (about 7% of volume) than 49% HF. Because it also contains about 38% NH$_4$F and it is acidic, it presents the toxic hazards of 49% HF.

TOXICOLOGY

- On contact, HF easily passes through skin and tissue. Because its action can be delayed for many hours, it can distribute throughout the body.
- Negatively charged fluorine ions bind very easily to positively charged calcium and magnesium ions to form insoluble salts. In the body, Ca and Mg ions are used to mediate a variety of physiological processes such as muscle movement. Calcium is also a chief component in bone. The capture of these ions by fluorine ions interferes with these important processes.
- Local tissue damage (at the point of contact) results from free hydrogen ions which cause corrosive chemical burns and from free fluorine ions which cause deep tissue damage, including erosion of bone.
- Systemic damage can occur when fluorine becomes distributed throughout the body. These conditions include hypocalcaemia (loss of calcium) and hyperkalemia (too much potassium). Since calcium and potassium regulate heartbeat, irregular heartbeat and cardiac arrest are possible! Deaths have been reported from concentrated acid burns to as little as 2.5% body surface area.
- Pure hydrogen fluoride is an extremely toxic gas which very easily dissolves in water. This solution is hydrofluoric acid. HF easily passes between the gas and liquid phases, so HF- and NH$_4$F-containing solutions will emit toxic fumes. Avoid inhalation of the fumes by always working inside the acid fume hood (never in the flow benches).
- Exposure to HF is treated by applying Calcium Gluconate gel (e.g., Calgonate® Gel). (This is a time sensitive material and shall be replaced before expiry.) This gel provides calcium ions which can scavenge free fluorine ions before they penetrate and damage tissue. In cases where systemic damage is a risk, calcium gluconate is administered intravenously by a healthcare professional.
- All personnel working in labs which use HF (including personnel who do not use HF themselves) shall read and familiarize themselves with the Calgonate® first aid instructions for hydrofluoric acid exposure (http://www.calgonate.com/safety_info.php), which are hereby incorporated into this SOP by reference.

PREPARATION

- Consult with a Chemical Hygiene Officer and register with the Chemical Safety program for highly toxic/dangerous substance.
- Do not handle HF while working alone in the cleanroom area.

DPS emergency number 213-740-4321
• Identify the locations of safety equipment (Eyewash and Shower station, Emergency Buttons and Phones, Absorbent Paper, 2.5% Calcium Gluconate ointment, Magnesium Sulfate, Sodium Bicarbonate Solution, Hazardous Waste Container, Acid Drain).
• Save DPS emergency line 213-740-4321 into personal phone.
• Prior to working with HF, read the Safety Guideline and Material Safety Data Sheet.
• Remove all hand and wrist jewelry. Do not wear contact lens (Contact lens are not permitted in the cleanroom).
• Wear all appropriate PPE (Splash Goggles, Face Shield, Rubber Apron with long sleeve, Acid Boots, two layers of disposable gloves, one layer of long butyl gloves over the disposable gloves, and one final layer of neoprene gloves over the long butyl gloves.
• Tuck cleanroom gown sleeves into glove cuffs. Double-check PPE before each use and ensure there are no pinholes on gloves.
• HF & BOE should only be kept in Polyethylene, Polypropylene, Teflon or Nalgene containers because they will etch silicon-based containers (glass & pyrex are SiO2-based).
• Immediately wash and decontaminate gloves that come into direct contact with HF.
• Ensure an adequate supply of clean-up material is within reach in case of spills.
• Ensure an appropriate waste container is accessible to dispose contaminated clean-up material.
• Restrict access to work area with sign labelled “Danger - HF Work Area”.
• Line work surfaces with plastic-backed absorbent paper (HF must be handled under a chemical fume hood).
• Clearly label all containers with any liquids, including containers with water.
• Clearly label all acid containers with full acid name and abbreviation, “Hydrofluoric Acid (HF).”
• Place containers with HF into secondary polypropylene container while not in use.
• When diluting HF, always add HF to water slowly (Do NOT add water to HF).
• Perform dry run of process.

WASTE DISPOSAL

• Dispose liquid HF waste in polyethylene bottle labelled as “CHEMICAL/HAZARDOUS WASTE CONTAINER.” “CHEMICAL/HAZARDOUS WASTE CONTAINER.”
• Wash and decontaminate all beakers and cylinders used in handling HF.
• Dispose liquids used in washing and rinsing beakers and cylinders into acid waste drain. DO NOT dispose concentrated acids into acid waste drain.
• Wipe off any visible HF droplets on surfaces.
• Remove any residual HF by washing with water. If washing is not practical, wipe down with sodium bicarbonate solution.
• Store HF-contaminated waste, including used disposable gloves, in chemical/hazardous waste container.
• When work is completed, remove and store PPE in the work area to prevent cross contamination.

SKIN AND EYE EXPOSURE

• Any bodily exposure to HF is to be considered an emergency requiring immediate action. It is ESSENTIAL to IMMEDIATELY employ the safety shower/eyewash in the event of being splashed with HF. Contaminated clothing MUST be removed under the shower even though
that may be embarrassing. Significant hydrofluoric acid contamination of skin may result in death or irreversible serious injury unless removed with the utmost speed.

- For skin and eye exposure to HF, immediately flood eyes and affected body area with cool water for a minimum of 15 minutes. Remove contaminated clothing and footwear while rinsing. Remove goggles last.
- For skin exposure, rinse in safety shower for 5 minutes and wear gloves to gently rub 2.5% Calcium Gluconate ointment onto affected area. Continue applying until emergency medical assistance is provided. Remove contaminated clothing and footwear while rinsing. Remove goggles last.
- Call or request other users to call DPS for medical assistance. Be sure to indicate exposure to HF. Double-bag contaminated clothes.
- If possible, submerge the affected area in iced or cool water while transported to an emergency room.

**INHALATION EXPOSURE**

- Move to location with fresh air.
- Call DPS for medical assistance

**ACCIDENTAL SPILLS**

- Do not attempt to clean large spills, especially if HF vapor results in noticeable eye or respiratory irritation.
- Clean up very small quantities of dilute HF only if you have been properly trained. Otherwise, call DPS and alert cleanroom staff.
- Labs using hydrofluoric acid shall have a hydrofluoric acid compatible spill kit. Absorbents must be rated by the vendor as suitable for hydrofluoric acid. Recommended absorbents are:

  1. PIG® Hydrofluoric Acid Neutralizing Loose Absorbent, 10 lb container.
  2. Amphomag®. Hydrofluoric acid labs should keep ≥ 25lb on hand. Note that this material is also suitable for dealing with spills of almost any liquid, not just hydrofluoric acid. The only downside is that there may be appreciable heat evolution when neutralizing concentrated acid.

**UNATTENDED EXPERIMENTS**

- Chemicals may not be left unattended for more than 15 minutes.
- For unattended experiments longer than 15 minutes, notify cleanroom staff to get permission.
- The maximum time for unattended chemicals is one hour.
- HF is highly hazardous and requires displayed signage at fume hood.
- The sign must contain the hazards of the experiment, the experimenter’s name and contact information, responsible PI’s name and contact information, Expected date and time of disposal.
- For more information on unattended highly hazardous experiments, please refer to the [Unattended Hazardous Operations Fact Sheet](#).

DPS emergency number 213-740-4321
EMERGENCY NOTIFICATION

- Notify the Department of Public Safety (DPS) at (213) 740-4321 or (323) 442-1000. For a non-emergency, dial (213) 740-6000.
- State the nature of the emergency (e.g., injury, hazardous materials or biohazards spill, fire) and provide details.
  a) Location of injury/incident
  b) Name(s) of injured and name(s) of witness(es)
  c) Contact information (your name and call-back number)
  d) Injury/incident summary
- Notify EH&S immediately at (323) 442-2200 or injuryprevention@usc.edu to report the injury/incident.
- Notify the cleanroom staff and your supervisor.

References

- SOP – HF and HF Precursors – USC EH&S
- HF Exposure Treatment Guide for Physicians – USC EH&S
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