Lab Safety and Procedures

SMIF Safety Policy

The Management and Staff of the Duke University Shared Materials Instrumentation Facility (SMIF) have implemented all reasonable measures to ensure that the facility provides a safe working environment. It is the responsibility of all users and staff to act in a professional, courteous, and safe manner at all times while in the facility.

Users violating the operating and safety rules of the facility or endangering the safety of themselves or other users, will be denied further access to the laboratory.
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Appendix: Recommended Medical Treatment for Hydrofluoric Acid Exposure
1.0 General Procedures

1.1 Location

The SMIF clean room and characterization lab facilities are housed on the first floor of the west wing of the Fitzpatrick CIEMAS building.

1.2 Lab Access and Equipment Use Certification

Access instructions and forms, equipment operating procedures, equipment certification checklists, and this safety manual can be downloaded from the SMIF web site: http://smif.pratt.duke.edu

To gain access to the SMIF facilities and equipment, users must follow the steps shown below. Access to the SMIF labs is by card entry using Duke ID cards. **Users must be certified by a SMIF staff member in order to use any equipment on their own.**

**Duke Users**

1. Contact your PI or Grant Manager to get set-up in the CoreResearch@Duke system.
   - Instructions for doing this can be found at [http://sites.duke.edu/coreresearch/training-materials/](http://sites.duke.edu/coreresearch/training-materials/). Scroll down to find the guide for “How to Add a Facility User and Link to a Project”
   - Note: Only the PI or grant manager of the fund code can set you up in CoreResearch@Duke. SMIF does not have the ability to do this.

2. Review this SMIF Lab Safety and Procedures manual

3. Go to the SMIF Training Class Calendar ([http://smif.pratt.duke.edu/calendar](http://smif.pratt.duke.edu/calendar)) and sign up for the appropriate safety and procedures classes
   - All users must complete the SMIF General Lab Safety and Procedures class
   - Cleanroom users must also complete the Cleanroom Safety and Procedures class
   - Chemical Hood users must also complete the Wet Hood Training and Chemical Safety class

4. Schedule training for the equipment you are interested in using by one of the following methods:
   - Check the SMIF Training Class Calendar (need link) to see if a training class is offered for the equipment you are interested in
   - Go to the appropriate Equipment and Procedures page (need link) and click on the primary training contact name to send an email requesting training.
• Train with a current certified user (e.g., someone from your lab who has been certified to use the equipment). Note – SMIF labor fees are not charged for this option

5. Contact the appropriate SMIF staff member to request certification on the equipment

6. Following certification you will be authorized to use the equipment on your own, and will be given access to the equipment reservation calendar.

**External (Non-Duke) Users**

1. Complete the SMIF External User Access Form (need link). Return a signed copy to SMIF via email to smif@pratt.duke.edu or fax to 919-660-5491

2. SMIF utilizes a system called CoreResearch@Duke for equipment scheduling and billing. You will need to be set up in this system in order to access SMIF. The steps for getting you set up are:
   - SMIF will request a Guest Account for you. Duke OIT will send you an email requesting information from you. Follow the instructions in the email to submit your information. Duke OIT will email you and copy the SMIF Director with your Duke NetID and UniqueID once they are assigned.
   - If you are associated with an institution or company that was not previously set up in CoreResearch@Duke, SMIF will submit the information to get your institution or company added.
   - SMIF will notify you when you are completely set up in CoreResearch@Duke.

3. Review the SMIF Lab Safety and Procedures (need link) manual

4. Go to the SMIF Training Class Calendar (need link) and sign up for the appropriate safety and procedures classes
   - All users must complete the SMIF General Lab Safety and Procedures class
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   - Train with a current certified user (e.g., someone from your institution or company who has been certified to use the equipment). Note – SMIF labor fees are not charged for this option

6. Contact the appropriate SMIF staff member to request certification on the equipment
7. Following certification you will be authorized to use the equipment on your own, and will be given access to the equipment reservation calendar.

1.3 Lab Etiquette

- **Be considerate of other users**
  - Use respectful, courteous and helpful language when communicating with other users and SMIF staff. Loud, boisterous and intimidating language will be a violation of accepted workplace standards and is not appropriate.
  - Disruptive, discourteous and/or insubordinate conduct will not be tolerated.
  - Acting inappropriately (such as using profane, suggestive or abusive language) is a violation of accepted workplace standards and will not be tolerated.
  - Conduct that causes or threatens harm to others or that constitutes persistent, unwanted behaviors will not be tolerated and will be grounds for removal of access.

- Users have an obligation to one another and to the laboratory to minimize interference with other users and to maintain the quality of the laboratory and its equipment.

- **Food and Drink are not allowed in any of the Equipment Labs or in the Clean Room.** Food and drink are only allowed in the seating area at the end of the main hallway.

- **Clean-up your work areas after you are done**

- Do not store samples, tools, books, materials, etc. in the lab except where designated by the SMIF staff. (Per section 4.2) If additional storage space is required, you must contact the SMIF staff first.

- **Notify SMIF staff of any issues or questions** via email to smif@pratt.duke.edu

1.4 Hours of Operation

- The SMIF facilities are open to certified users during the following times:
  - **Clean Room Lab:** 7am to 12am 7 days/week
  - **Characterization Labs:** 24 hours/day* 7 days/week

*The acid and solvent wet hoods in the Offline/Sample Prep lab can only be used from the hours of 7am to 12am.

Per the above schedule, clean room users must exit the clean room prior to 12am, and card access is not activated until 7am.

- **After certification, users may work alone in the labs provided the following:**
  - They have been certified on all equipment that they will be using.
  - The work performed must be *Routine* for the user.
  - The user must understand the *Risks*.
  - The user follows all safety and laboratory procedures.
If using chemicals, there MUST be another person present in the lab. You may not wet etch, mix chemicals, or dispose of waste without another user in the area (See section 6.5.9 regarding the buddy system for chemical usage).

1.5 Computer Abuse

Computer abuse is a violation of university policy, and may subject the abuser to various disciplinary actions from SMIF management, the campus judicial system, and legal authorities. Abuses of the SMIF computers will have the same results as violations of SMIF safety rules ranging from denial of access to the computers for a period of time to permanent exclusion from the facility. Computer abuse includes, but is not limited to:

- Using SMIF computers without proper authorization, or for unauthorized purposes, including using or attempting to use an account not issued to you
- Tampering with or obstructing the operation of the SMIF computer
- Inspecting, modifying, distributing, or copying software or other data (whether this is system software, data, or files of another user) without authorization
- Downloading software onto SMIF computers without authorization from SMIF management

1.6 User Communication

All users must supply SMIF with a functional e-mail address that they check regularly for messages. E-mail will be the primary mechanism for notification of users of equipment and laboratory status information. Please notify SMIF staff if there is any change to your contact information that was given in your access form.

2.0 Consequences of Violating SMIF Rules and Policies

The consequences for violating SMIF rules and policies are outlined below:

- If a user is found to violate SMIF rules or policies:
  - They will be sent one warning e-mail (with their advisor copied) and will be put on “probation” for a period of 6 months
- If SMIF rules are violated a second time while on probation
  - Their SMIF access will be removed for 1 month
  - Probation period extends to 1 year
  - The e-mail notification of the violation to the user and advisor will be followed up with a written letter that requires a signed acknowledgement
- If SMIF rules are violated a third time while on probation
  - The user and their advisor will attend a hearing with the SMIF Advisory Committee and the length of expulsion from SMIF will be determined by the committee (minimum of 6 months)
  - The meeting will be followed up with a written letter that requires a signed acknowledgement
3.0 Alarms and Evacuations

3.1 Toxic Gas Monitoring System

The SMIF Facility has installed a sophisticated Toxic Gas Monitoring (TGM) system. This system senses the presence of dangerous gases and vapors and then annunciates the appropriate alarms and automatically shuts down the gas source. It is integrated with the CIEMAS building and fire alarm system.

3.2 Manual Alarm Buttons

Manual alarm buttons are located at all emergency exit doors in the clean room, as well as at each exit door in the characterization labs. These are blue boxes mounted on the wall with a push button in the middle. In the event of an emergency that is not immediately detected by the toxic gas monitoring system (such as a large chemical spill), users should immediately evacuate the area and press the manual alarm button on their way out the door.

3.3 Alarms Types and Evacuation Response

There are two types of alarms within the SMIF facilities:

**Flashing blue light with a continuous siren (TGM alarm)**
This is an indication of a local alarm caused by a detection event from the TGM system or from a manual alarm button activation. Upon hearing or seeing this alarm, you should immediately evacuate the area(s) where the alarm is sounding. If you have knowledge of the cause of the alarm or any other helpful information you should proceed to the SMIF office area and notify one of the SMIF staff members.

**Flashing white light with intermittent horn (Fire/Building alarm)**
This is an indication of a building wide alarm caused by the building fire alarm system or a high level detection event from the TGM system. Note that for the case of a high level detection event from the TGM system, both the TGM alarm and the fire/building alarm will annunciate simultaneously. Upon hearing or seeing this alarm, you should immediately evacuate the CIEMAS building and gather outside in the area between CIEMAS and Hudson Hall. If you have knowledge of the cause of the alarm or any other helpful information you should locate a SMIF staff member in the evacuation area to relay this information.

*Note to clean room users:* If an alarm sounds that requires you to exit the clean room you should immediately exit through the closest door (for example, at the end of the bay where you are working). You should not try to make your way to the gowning room and/or take the time to remove your clean room garment. Once safely outside the clean room or building, you may remove your garment. Once the alarm condition is over, please return your dirty garment to the pre-gowning area. (Do not take or wear it back...
inside the gowning room or clean room). You may get a new garment when you enter
the gowning room.

3.4 Summary

| Intermittent Horn with Flashing White Light: | Evacuate the CIEMAS building |
| Continuous Siren with Flashing Blue Light:  | Evacuate the affected area |

4.0 Equipment Use and Availability

4.1 Certified Users

Access to the laboratories does not of itself permit use of any particular instrument. You
must receive training and then be certified by SMIF staff to use any piece of equipment.

Much of the equipment in the facility is highly complex and delicate. We view hands-on
access as an important part of the educational process. Each instrument necessarily has
rules and operational procedures that are set by the staff to assure the safe and continued
operation of the instrument. Violation of these procedures or carelessness in operation
can result in damage to the equipment, downtime and considerable expense.
Consequently, careless or damaging use of equipment will result in suspension of user
privileges, either for a specific instrument or the facility as a whole.

Operating procedures for each tool can be found on the SMIF web site, and will be used
as the basis for training on a given tool. Users will be expected to understand and be able
to fully follow the operating procedure in order to be certified.

A few general policies for equipment usage are:
- Know where equipment operating procedures and manuals are located
- Do not touch or adjust any controls or settings that were not explained to you during
  training
- Leave all equipment in the appropriate state for the next user (as instructed during
  training)
- You must contact SMIF staff with any requests to modify or move equipment

4.2 Equipment Operations

SMIF uses the CoreResearch@Duke an on-line system for equipment scheduling and to
record usage in the clean room and on characterization equipment. SMIF specific guides
for using this system can be found at http://smif.pratt.duke.edu/reservations. General
help for CoreResearch@Duke is available at http://sites.duke.edu/coreresearch/.
4.3 Equipment Use Charges

One of the fundamental reasons for the creation of the Shared Materials Instrumentation Facility was to enable access for Duke University researchers to equipment that they do not have the resources to maintain and operate on their own. As with other university-based shared facilities, hourly user fees are charged as a means of recovering the direct costs associated with operating such a facility. These fees are reviewed by the Office of Sponsored Programs and approved by Duke’s central administration.

All Users (Duke, Non-duke University, federal, and industry) are charged hourly equipment or lab use fees. These fees are used to recover direct operating costs associated with the equipment and the laboratory (equipment and lab supplies, maintenance costs, labor to keep the tools running, etc.) Academic and non-academic users are charged at different rates. The current fees for each tool or lab are given on the SMIF web site at http://smif.pratt.duke.edu/user-fees-and-billing.

4.4 Equipment Scheduling

All SMIF equipment is reserved through the CoreResearch@Duke system. Users should understand the scheduling system and use it reserve time slots on instruments. Equipment is generally reserved on a first-come basis. You will be notified if there are certain sign-up restrictions on particular tools due to the level of usage. You must schedule time on equipment in advance.

**Important Things to Know about CoreResearch@Duke**

- CoreResearch works ONLY on **Chrome, Microsoft Internet Explorer, and Safari**. Mozilla FireFox is not a supported browser at this time.
- Login to CoreResearch@Duke by going to https://coreresearch.duke.edu/CR/logon.jsp You must have a Duke NetID and password to login and use CoreResearch@Duke
- SMIF bills you based on your actual usage of the instrument or lab. However, the system defaults to your reserved time for billing if you do not start/stop your reservation manually. **This also means that you will be billed for your reservation if you do not show up, unless you cancel the reservation ahead of time.**
- **If you can’t login to CoreResearch@Duke** (assuming you’ve entered your NetID and password correctly): this means you probably have not been set up with a fundcode/project. Only your PI or Grant Manager can set you up – this can’t be done by SMIF. For external (Non-Duke) SMIF users, please contact smif-billing@duke.edu to get set up in the system.
4.5 Equipment Problems

Problems with equipment malfunctions, breakage, etc. should be reported to the SMIF staff. **Do not try to fix or adjust anything yourself.** This equipment is very expensive and much of it is very delicate. Considerable damage can be done at a great cost of both money and downtime by careless attempts to fix things.

**Do not call the staff at home in the evenings or on weekends about minor problems with the equipment or your process or measurements.** Send an e-mail to smif@pratt.duke.edu and the SMIF staff will address the problem the next morning. Obviously, major problems like fire or smoke, or equipment alarms should be reported immediately using the emergency contact information posted near the phones in each lab.

Any emergency involving injuries, fire, chemical spills, etc., should be first reported to the Duke Police dispatcher by dialing 911 from any Duke phone or dialing 919-684-2444 from a personal cell phone. They in turn will contact the proper response organizations (e.g., the Duke Occupational and Environmental Safety Office (OESO)). There is always someone on call from Duke OESO.

5.0 General Laboratory Practices

5.1 Visitors

You are responsible for the actions and safety of any visitor that you bring into the SMIF facilities. A “visitor” is considered to be anyone who has not completed the SMIF Safety and Procedures training class, whether or not that person is affiliated with Duke University.

**No visitors are allowed to be taken inside the clean room lab without prior approval from SMIF management.**

You may take visitors inside the characterization labs, but you are encouraged to notify SMIF management first.

5.2 User Storage

A limited amount of storage space, in the form of small bins is available for users in the clean room lab. These should be used for keeping only currently needed substrates, masks, etc. Clean room users will be assigned a storage bin. These bins can be removed from the storage area within the clean room while using the lab, but must be returned to their storage area before you leave the clean room.

**No chemicals of any kind may be stored in the User Storage areas.** Chemicals are to be stored only in the designated chemical cabinets.
There are no user storage areas outside of the clean room. All users should remove samples and other items from these areas when they are done and store them in their own labs.

5.3 Phones

Users may use their personal cell phones while working in the SMIF facility. A cordless phone is provided in the SMIF cleanroom for the use of staff and users. This phone is not a substitute for office phones for users. Users should not routinely make or receive calls on the SMIF cleanroom phone. SMIF staff will not routinely take messages for SMIF users.

Phone numbers for the SMIF staff are posted at the entrances to the sample prep lab, the entrance to the cleanroom, and inside the cleanroom near the cordless cleanroom phone. Please only use the after hour numbers in case of equipment or facility emergencies.

For immediate response to emergencies involving safety or medical assistance (e.g., injury, chemical spill, etc.):

Dial 911 (from a Duke Phone number)
Dial 919-684-2444 (from a cell phone)

to reach the Duke Police dispatcher. They in turn will contact the proper response organizations (e.g., the Duke Occupational and Environmental Safety Office (OESO)).

5.4 Buddy System

A “Buddy System” is in place for all chemical use in the SMIF facilities. (See section 7.5.9) For the buddy system, a knowledgeable user must be in the lab to assist you in an emergency. Additional procedures may apply to specific instruments. You will be advised of these when you are trained on each instrument.

6.0 Clean Room Practices

6.1 Protocol for Contamination Control

The primary limitation to clean room cleanliness is the people using the clean room. Strict adherence to our rules and common sense will allow us to maintain a level of cleanliness adequate for the types of work done in the SMIF clean room.
You are the biggest source of contamination in the clean room. Your clothes, your feet, your skin, and your hair produce particulates that may compromise your research goals.

Clean Room Rules and Restrictions

- **Do not** bring anything into the clean room that is not absolutely necessary for the work you are doing.
  - You should leave all coats and jackets outside the clean room on the hallway coat rack
  - Backpacks, purses and other items can be securely stored in the lockers located in the SMIF hallway across from the large whiteboard. These lockers are for storing items only while you are in the cleanroom, and must be emptied when you leave the cleanroom.
- **Items that are not allowed in the gowning room or clean room include:**
  - Food, drinks, or gum
  - Paper (special clean room paper lab-books can be purchased from SMIF for use in the clean room)
  - Cardboard or any other packing material
  - Pencils, erasers, or felt-tip markers
- **You must clean off any items** (sample carriers, equipment, parts, tools, etc) before bringing them into the clean room. Wipes and cleaning solution are located in the gowning room for this purpose.
- **Activities that are not allowed in the gowning room or clean room include:**
  - **Do not** wear make-up.
  - **Do not** comb your hair in the clean room or gowning room.
  - **Do not** run or engage in “horseplay”

6.2 Clean Room Attire

- Prior to entering the gowning area of the clean room you should ensure the following:
  - **Do not** wear dirty clothes; particularly muddy boots or shoes into the clean room
  - Bare legs should be covered.
  - Socks or nylons should be worn along with closed toe shoes that completely cover the foot.
- **Entrance and Donning Sequence**
  - Enter into the pre-gown area
  - Log in for clean room usage using the sign-in computer

  *Note: Each user must independently log into the clean room using the sign-in computer. Users that enter the clean room without logging in will have their access revoked.*
  - Use your Duke card to enter the gowning area
  - Immediately put on a pair of Nitrile gloves
  - Put on your clean room garment, dressing from the head down:
    - Cleanroom hood with mask
- Cleanroom coverall
  - Take care not to drag the legs on the floor.
  - Be sure that hood is tucked into Coverall
  - Fasten the zipper completely up to the neck
  - Fasten snaps and all buttons on the suit
- Cleanroom booties
  - Snap to the coverall and/or adjust the top of the shoe to be snug around the calf.
- Safety glasses or goggles
  - Attach your identification badge to the outside of the coverall
  - Walk across the second tacky mat before entering the cleanroom

*You must have your cleanroom identification badge displayed on your garment at all times while working in the cleanroom*

- Exit and Doffing Sequence
  - When exiting the cleanroom and still within the gowning room, remove the garments as follows (bottom up):
    - Remove booties and snap to bottom of leg of coverall
    - Remove coverall and hang on your designated hook
    - Remove hood and snap to top of bunny suit
  - When garments require cleaning, place the garment in the laundry container
  - When exiting the gowning room and still within the pre-gowning area, remove your gloves and discard them in the waste container.
  - Log out your clean room usage using the sign-in computer

### 6.3 Clean Room Services

Compressed air, laboratory vacuum, house (dry) nitrogen, and de-ionized (DI) water are supplied in the clean room.

- **Compressed air** is used only for pneumatic valves on equipment.
- **Laboratory vacuum** is used only for spinners and chucks.
- **House nitrogen** is clean, dry nitrogen obtained from the boil-off of liquid nitrogen in a storage tank. It is used for venting vacuum systems, for vacuum pump purges, and for N2 guns (blowing off or drying substrates)
- **De-ionized water** is available in the chemical benches. Please do not leave DI faucets or cascade rinse tanks running unnecessarily.

### 6.4 Areas off limits to users

Users are not allowed to enter the following areas without permission from SMIF:
- Chases (mechanical areas between the equipment bays)
• Equipment move-in (area through the double doors to the left)
• Gas/Chemical storage room

6.5 Clean Room Monitoring

All entries into the cleanroom are monitored via card reader swipe records and the computer logins to insure that users are logging in as appropriate and entering and exiting the cleanroom during the appropriate hours.

Activity within the cleanroom is also monitored for safety and security reasons using video camera placed around the lab.

7.0 Personal Chemical Safety

7.1 Safety Overview and Philosophy

Safety is the primary concern in all SMIF laboratory activities. All operations must be undertaken with the safety of both the individual user and other users as the primary consideration. Operating safely is more important than getting your project done. As a general rule, anyone violating any safety rule or otherwise compromising his or her personal safety or the safety of others will be denied access to the laboratory.

All users should read through the Duke Laboratory Safety manual (specifically the sections on Chemical and Fire Safety) and complete the on-line laboratory safety training offered by the Duke Occupational and Environmental Safety Office at www.safety.duke.edu.

Many chemicals and gasses used in the SMIF labs are extremely hazardous. They can cause severe and permanent damage to human tissue, resulting in serious injury or even death. It is each user’s responsibility to be alert and cautious when using these chemicals and gases and to avoid all contact with them. Following the safety procedures will minimize your risk of injury.

For the most part, rules on chemical use are formulated on the basis of basic chemical knowledge, the properties of individual chemicals, and common sense. In addition, a large volume of state and federal law covers chemical use in the workplace and disposal of waste. In spite of rules and staff supervision, primary responsibility for safety rests with the individual user. A responsible, considerate user with an understanding of basic chemistry, common sense, and an instinct for self-preservation will have little trouble with our chemical rules or chemical safety.

Your safety in the laboratory is determined not only by your actions but by the actions of those around you. Since the staff is in the laboratory only a portion of the time the facility is open, the users are often in the best position to observe the behavior of others. You are
encouraged to point out rule violations immediately to the offenders, as well as to the staff at the first available opportunity. The access of everyone to the facility depends on maintaining a safe working environment.

We also welcome your suggestions regarding safety and laboratory procedures. Please notify SMIF staff immediately of any safety concerns.

7.2 Laboratory Hazards

Hazards in the laboratory fall into two general categories; compressed gases and wet chemicals.

Compressed Gases
The facility uses a variety of compressed gases, some of which are toxic, highly toxic, corrosive, flammable, or explosive. The use of these gases is thus strictly regulated. An accident with any of these could be catastrophic. These hazards, however, can and have been minimized by the proper use of engineering controls, such as the use of proper equipment, proper confinement, ventilation, sensors, purges, safety valves, etc., and by procedural controls implemented by the staff. These will be discussed more in the section on gas safety.

Wet Chemicals
The second, more troublesome category of hazard, concerns wet chemicals, i.e. the acids, bases and solvents commonly used in etching, cleaning and lithography. These are “hands on” hazards and, in a multi-use facility like ours, are harder to control by engineering. The chemicals we commonly use in this facility can cause severe burns, tissue damage, organ damage, asphyxiation, and genetic damage if improperly used. These chemicals can enter the body by inhalation, ingestion, or absorption (either directly through the skin or through gloves) and may have either long or short-term health consequences. Mixing of incompatible chemicals (such as oxidizers and organics) can cause reactions and/or fires/explosions. In addition, improper use of solvents can result in a major fire. These concerns will be covered more in a later section. Users are expected to treat all chemicals with appropriate respect, and to be aware of all possible reactions that may be created, either intentionally or by accident.

7.3 Sources of Chemical Information

The Safety Data Sheet (SDS) is a convenient, condensed source for information on the properties of any chemical. The SDS is a federally mandated document that must be
supplied to you by the manufacturer or distributor of a chemical. It contains in summary form, the chemical composition, the physical and chemical properties, toxicology data, and instructions for handling, spill control, and waste disposal. You must read the SDS for any chemical you use in SMIF. Safety data sheets for all chemicals approved for use in SMIF are available on-line through the SMIF web site, or can easily be found by typing the chemical name and “SDS” (or the older term “MSDS”) into an internet search engine.

7.4 Terminology

The following terms are often encountered when reading about the properties of chemicals and the toxicity of chemicals. Simple definitions are included here to help you understand the properties of common chemicals when referring to the SDS or other references. This is not intended to be a complete reference on Toxicology or Chemical Safety.

7.4.1 Chemical Properties Terms

- **Corrosive** chemicals are those that cause visible destruction of, or irreversible alterations in, living tissue by chemical action at the site of contact. Examples of corrosive chemicals include strong acids and strong bases.
- **Flammable** materials include aerosols, gases, liquids, and solids. Flammable gases can form a flammable mixture with air. Flammable liquids refer to any liquid having a flashpoint below 100°F.
  - Flash point is the minimum temperature of a liquid at which it gives off sufficient vapor to form an ignitable mixture with air. Liquids with a flash point near room temperature can be ignited very easily during use.
- **Oxidizers** are chemicals that make combustible materials and liquids burn easier and with more intensity. For this reason, oxidizers should never come in contact with solvents or acetic acid. Examples of oxidizers in SMIF include Hydrogen Peroxide, Nitric Acid, and “Piranha” solution.
- **Pyrophoric** chemicals spontaneously ignite in air. No source of ignition (spark) is needed. They react spontaneously when exposed to oxygen. Silane is an example of a pyrophoric gas.
- **Exothermic Reaction** is a reaction that produces heat (releases energy).

7.4.2 Types of Exposure

- **Acute Exposure** as used in toxicology refers to a short-term exposure. It has nothing to do with either the severity of the exposure or the severity of the effect. The type of exposure occurring during an accidental chemical spill is properly described as an acute exposure.
- **Chronic Exposure** as used in toxicology refers to a long-term exposure. Again, it has nothing to do with the severity of the exposure, the severity of the consequences, or the duration of the consequences. Chronic exposures can be the result of chemicals in
the workplace, the home, or the environment. Chronic exposures are usually the result of carelessness, ignorance, or neglect, and not the result of an accident.

- **Local Exposure** refers to exposure limited to a small area of skin or mucous membrane.
- **Systemic Exposure** means exposure of the whole body or system, through absorption, ingestion, or inhalation.

### 7.4.3 Types of Effects

- **Acute Effects** refers to the duration of the symptoms. Acute means symptoms lasting a few hours or days. Again, it has nothing to do with the severity of the effects.
- **Chronic Effects** are long-term effects, manifested by prolonged duration and continuing injury.
- **Local Effects** occur in a small area, at the place of contact.
- **Systemic Effects** occur throughout the body, or at least away from the point of contact.
- **Allergies and Hypersensitivity** are reactions by particular individuals to particular chemicals, caused by heredity or prior overexposure. Hypersensitive individuals should avoid exposure to the offending agents.

### 7.4.4 Exposure Levels

- **TLV-TWA (Threshold Limit Value - Time-Weighted Average)** - This is the (averaged) level to which you can be exposed 8 hours a day, 5 days a week for a working lifetime, without adverse health effects. These levels are set by ACGIH (American Conference of Governmental Industrial Hygienists). This level is most relevant to chronic (long term) exposure to chemicals in the workplace.
- **IDLH (Immediately Dangerous to Life and Health)** - This level represents any condition that poses an immediate threat of loss of life; may result in irreversible or immediate-severe health effects; or may result in eye damage; irritation or other conditions that could impair unaided escape. It is the value most appropriate to sudden, one time accidental exposures.
- **STEL - Short Term Exposure Limit** - Maximum concentration to which you can be exposed for 15 minutes, up to 4 times a day without adverse effects.
- **PEL - Permissible Exposure Limit** - The statutory equivalent of TLV.
- **LD50** - The dose at which 50% of those exposed will die. Separate levels apply to various modes of exposure (inhalation, dermal, etc.)

### 7.4.5 Toxic Effects

- **Carcinogen** - A substance producing or inciting cancerous growth.
- **Mutagen** - Capable of inducing mutations.
- **Teratogen** - A substance causing damage or death to a fetus.
• **Acute Toxicity** – Some chemicals can cause acute toxicity to targets organs. For example, nitric, sulfuric, and hydrofluoric acids are highly corrosive to the skin and mucous membranes. Hydrofluoric acid can also cause decalcification of bones.

### 7.5 Chemical Use

Users must attend the Wet Hood and Chemical Safety class and be trained and certified on chemical hood usage before using the chemical hoods. Chemicals are to be used ONLY in the exhausted chemical hoods.

#### 7.5.1 Chemical Authorization

Only specifically authorized chemicals may be used in the SMIF laboratories. Many standard chemicals have been pre-authorized.

No other chemicals may be brought into the facility without the specific authorization of SMIF. SMIF may issue approval based on a review of the SDS and other relevant information provided by the user. Approval of new chemicals is not guaranteed, as certain chemicals may not be allowed if they are too hazardous or are incompatible with other uses of the laboratory.

You should obtain approval **before** buying or ordering a chemical. **Do not show up with chemical in hand expecting instant approval.** Chemicals must not be brought and left in the facility awaiting approval.

Once approved by SMIF staff, all chemicals must be labeled with the following:

- Name of chemical as it appears on the SDS
- Physical and health hazards of the chemical
- Contact information for the main owner/user of the chemical when applicable

Once a chemical is approved, SMIF will contact you to verify proper storage, use, and disposal of the chemical.

#### 7.5.2 Chemical Practice

A little bit of common sense and courtesy when using chemicals will make the laboratory safer and make it easier for the staff to monitor chemical use.

- You must clearly and legibly label all chemical containers (beakers, etc) with your name, the chemical name, hazard class (corrosive, flammable, etc) and date if that container will be left in the hood for any length of time without you immediately present at the hood. The following chemical hazard labels are provided by SMIF:
Corrosive – may cause severe skin burns

Oxidizer – may cause or intensify fire

Causes serious eye or skin irritation

Flammable

Health Hazard – may cause cancer, fertility issues, or organ damage

Fatal if inhaled, swallowed, or in contact with skin

• Users are NOT allowed to use chemicals that have someone else’s name on them without the permission of the chemical owner.
  o SMIF supplies para-film and a marker that can be used to seal personal chemicals and protect them from unauthorized usage
• Do not leave any unlabeled chemical containers in the hoods, even for “just a minute”.
• Chemicals must be properly disposed of as soon as you are finished.

These procedures are necessary to allow us to identify chemicals left behind, spilled, or forgotten.

Since we have a limited amount of chemical hood space, cooperation by users is required. If there is more than one user working in a hood, the first user in the hood has the option to exclude others from the area while he/she is working, for either safety or process reasons.

7.5.3 Lab-ware

SMIF provides glassware and plastic ware for all to use in the laboratory. You are not authorized to appropriate a private stash for your own use. Users are encouraged to purchase their own lab-ware for their private use if cross-contamination is a concern. All lab-ware should be thoroughly cleaned and rinsed after use and properly stored. Private use lab-ware should be stored in your individual user storage.
Do not dispose of glass or contaminated materials in the regular trash. Contact SMIF staff if there are any questions regarding proper disposal of materials. Glass should be disposed of in proper broken glass containers.

7.5.4 Chemical Hood Operation and Rules

All chemical operations are to be done in the chemical benches. You should perform your work well inside the hood, away from the front edge. However, you should never stick your head inside a chemical hood in order to reach something at the back of the hood. If you are using the hoods properly, you should not be able to smell chemicals outside the hood.

You are expected to clean up after yourself. Do not leave beakers, wipes, etc., or chemical or liquid residue in the wet hoods. The work surface should be clean and dry when you start, and clean and dry when you leave. The next user has no idea if that puddle of clear liquid is HF or just water.

Keep solvents and acids separated.
- Acids are to be used ONLY in the white color polypropylene chemical hoods.
- Solvents are to be used ONLY in the stainless steel chemical hoods. Water is not allowed in these hoods.

Keep solvents and oxidizers separated
- Oxidizers are to be used ONLY in the white color polypropylene chemical hoods
- Solvents are to be used ONLY in the stainless steel chemical hoods.

Acetic Acid is an exception – it should be used in a Solvent Hood and stored in a Solvent Cabinet
- Because Acetic acid is incompatible with oxidizers and many acids, it should be stored in a solvent cabinet and used in a solvent hood

Photolithography chemicals are to be used only in the clean room Photo Bay areas
- Photoresist and spin on organics are to be applied only in the designated spin modules within the spin coating hoods
- Developer solutions are only to be used in the developer (base) chemical hood

Understand the proper disposal of any chemical with which you are working. (See section 7.7).

7.5.5 Hot Plates

While you may think hotplates are mundane, they can in fact be very dangerous when used in chemical hoods. Fires and melt down of the plastic hoods are both significant concerns. The following rules apply to hotplate use:
- **Hot plates used for heating chemicals must be attended.** You must be in the laboratory and near the hot plate whenever it is powered on.
- You may not heat solvents with flashpoints of <130 F.
7.5.6 Personal Protective Equipment

When using chemicals, users must minimally wear the following items:

**Clean Room Laboratory**

<table>
<thead>
<tr>
<th>For Acid Use</th>
<th>For Solvent or Spin Coating Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>In addition to the standard clean room attire, the following items are to be worn:</td>
<td>In addition to the standard clean room attire (including nitrile gloves), the following items are to be worn:</td>
</tr>
<tr>
<td>• Chemical Apron</td>
<td>• Safety Goggles</td>
</tr>
<tr>
<td>• Safety Goggles</td>
<td>• Users should “double” glove when using chlorinated solvents.</td>
</tr>
<tr>
<td>• Chemical Face Shield</td>
<td></td>
</tr>
<tr>
<td>• Chemical Gloves</td>
<td></td>
</tr>
</tbody>
</table>

**Offline/Sample Preparation Laboratory**

<table>
<thead>
<tr>
<th>For Acid Use</th>
<th>For Solvent Use ONLY</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Chemical Apron</td>
<td>• Safety Goggles</td>
</tr>
<tr>
<td>• Safety Goggles</td>
<td>• Lab gloves (nitrile). Users should “double” glove when using chlorinated solvents</td>
</tr>
<tr>
<td>• Chemical Face Shield</td>
<td>• Lab coat (optional)</td>
</tr>
<tr>
<td>• Chemical Gloves</td>
<td></td>
</tr>
</tbody>
</table>

- Check chemical gloves for holes.
- Wash gloves when contaminated.
- Wash gloves before removal.
- Wear gloves to open chemical cabinets.
- Wash and remove gloves before touching anything else (door knobs, notebooks, phone, microscopes, etc.)

The aprons, face shields and chemical gloves are to be worn only at the hoods. They must be removed when using other equipment in the laboratory.

7.5.7 Chemical Supplies and Storage

SMIF stocks and supplies the chemicals commonly required for processing in the facility. Users are neither allowed to bring in their own stocks of these chemicals or to appropriate as a private stash any of these chemicals. We do not have room for people to have private bottles of commonly used chemicals.

We have very limited chemical storage for user specific chemicals. You may also not store custom solutions without staff approval. Mix only as much of these as you need each day. All special chemicals and solutions must be labeled with the arrival date and the owner’s name. SMIF annually inventories all chemicals being stored in the chemical
cabinets, and following notification of users, will properly dispose of any chemicals no longer in use.

Working stocks of chemicals are kept in the chemical cabinets near each chemical area. Users must not open a new bottle until the old one is empty. When you empty a chemical bottle, do not return it to the chemical storage cabinet.

- Empty acid bottles should be thoroughly rinsed out with water, and the empty bottle left in the chemical hood for disposal by SMIF staff. (Rinse water may be safely disposed in the normal drain).
- Empty solvent bottles should be placed in the solvent chemical hood with the cap off and allowed to dry. SMIF staff will then properly dispose of the empty bottle.

### 7.5.8 Pregnancy

If you and your spouse or significant other are planning a pregnancy, you are strongly encouraged to use the “Reproductive Health” resources through Duke University’s Occupational and Environmental Safety Office. This information can be found at the following web site:

http://www.safety.duke.edu/OHS/ReprodHealth.htm

Users who believe themselves to be pregnant should discuss laboratory use with the SMIF director as soon as possible. This need not severely restrict laboratory use but should nonetheless be discussed. (See discussion of solvents in photoresist in section 7.6.5.)

### 7.5.9 Buddy System for Chemical Usage

A buddy system applies to the use of wet chemicals in any of the SMIF facilities. These rules apply for chemical usage when SMIF staff is not present, which includes weekends and holidays, and Mon-Friday from 5pm to 12 midnight. *Chemical usage of any kind is not allowed between the hours of 12 midnight and 7am.*

The buddy system requires that another knowledgeable user be in the laboratory, aware of your situation, and close enough to be of assistance if you have an accident. He or she need not be constantly at your side, just available and aware.

#### Using Chemicals in the Cleanroom

- Another person must be in the cleanroom and aware that you are using chemicals
- Exception: You may use the hoods in the Lithography area (spin coating, develop, and solvents) without a buddy present

#### Using Chemicals in the Sample Prep Lab

- Another person must be in the sample prep lab and aware that you are using chemicals
7.5.10 Contact Lenses

In the past, it was not considered good laboratory practice to wear contacts in any laboratory. Recently the American Chemical Society has changed its recommendation, and SMIF has adopted its practice. Contact lenses may be worn in the laboratory, provided that appropriate supplemental eye protection is worn when actually using chemicals. In SMIF, this would be the goggles and full-face shield when using acids and goggles when using solvents and lithography chemicals.

7.5.11 Emergency Response Equipment

Spill kits and spill control pillows are available in the laboratory for absorbing liquid chemical spills. They are located near the chemical hoods.

Emergency showers and eyewashes are located near all chemical hoods in the clean room and offline/sample preparation lab. Most chemical burns, particularly in the eyes, should be washed for 20 minutes before seeking further medical attention.

First Aid Kits are located in the clean room on the main aisle and in the offline/sample preparation lab.

Calcium Gluconate Gel is available at all of the Acid Hoods for application to HF skin exposures. This should be applied promptly, but is not a substitute for prompt medical attention.

7.5.12 Chemical Accidents

The following actions should be taken in the event of a chemical spill:

Spills Contained Inside a Chemical Hood
- Avoid breathing vapors from the spill and leave the immediate area of the chemical hood
- Alert people in the immediate area of the spill
- Notify SMIF immediately by calling emergency numbers posted near the phone
- Wait for instructions from SMIF or for SMIF personnel to arrive to complete the clean-up of the affected area.

Spills Outside of a Chemical Hood
- Attend to injured or contaminated persons and remove them from exposure
- Press the closest manual alarm button (blue box) and evacuate the lab
- Make yourself available to the SMIF staff and/or emergency responders and be prepared to tell the following:
  - What chemical(s) are involved
  - How much was spilled
  - Where the spill is located
  - Nature of any injuries
All accidents involving chemicals and all accidents involving personal injury must be reported to the SMIF management in writing (e-mail) as soon as possible after the incident. Explanations should include the nature of the event, the procedures being followed or not followed at the time, and suggested actions for preventing future similar incidents. All injuries should also be reported within 24 hours to Workers’ Compensation, via a form available on the HR website: http://www.hr.duke.edu/forms/injury.html.

7.5.13 Reminders and Final Checklist

Common sense is the most valuable aid you have in working with chemicals. If you are unsure about any aspects related to the chemicals you will be using, do not use them before asking the SMIF staff for assistance. It is impossible to enumerate all the rules and cautions applicable to chemical use, but here are a few more to consider:

- Always pour chemicals slowly to avoid splashing
- When mixing, always pour acid into water – never pour water into acid
- Completely rinse any used glassware or Teflon containers
- Perform all chemical operations carefully; especially moving, mixing, and pouring
- Open chemical containers must remain under the hoods. Move them around inside, not outside
- Keep your head outside the hood enclosure at all times
- Don’t sit down at the hood, it puts your face directly in the fume path
- Finish open chemical bottles before opening new ones
- Don’t use N2 blowguns near open chemicals
- Don’t use plastic beakers on hot plates
- Clean up after yourself and be careful

7.6 Specific Chemical Hazards

7.6.1 Acetone and Flammable Solvents

Acetone is widely used throughout the facility. It is a very flammable solvent with a low flash point, (i.e. it can be ignited at a low ambient temperature). Because of this it presents a significant fire hazard. A spill of a gallon bottle of acetone could cause a catastrophic fire or explosion. It should not be transported except in chemical buckets. Solvents should also be handled with care in the hoods and not used near hot plates. Spilled solvent can be ignited by the hot plates. Spilled solvents can react explosively with chemical oxidizers present, e.g., peroxides or nitric acid. Spilled solvents should be contained immediately with spill control pillows.

7.6.2 Hydrofluoric Acid

Hydrofluoric acid, HF, presents a significant hazard for personal injury. It is used in the lab in its pure form, diluted, and as the active component of BOE, Buffered Oxide Etch. It is used for etching silicon dioxide and particularly for stripping the native oxide prior
to further processing. HF, however, is a very hazardous chemical, much more so than any of the other acids. At the concentrations typically used in the laboratory, an HF “burn” may be initially painless. The acid however will silently eat away at your flesh and the damage will penetrate deeper and deeper, until it comes to the bone. This can result in irreversible tissue and bone damage as well as fluoride poisoning, and at some point, if left untreated, you may die.

**HF Potential Hazards**
- Liquid HF is one of the strongest and most corrosive acids. It can be irritating to the skin, eyes, and respiratory tract. Contact with exposed body parts can cause painful burns and even death.
- In high concentrations (more than 50%), HF usually causes immediate burns that are extremely painful and slow to heal.
- In lower concentrations, exposure may not be apparent for several hours, but can still cause burns and further damage if not washed off.
- HF causes such severe burns because it penetrates beneath the skin and dissociates into hydrogen and fluoride ions. When fluoride ions bind with calcium in the body, it can result in tissue destruction, decalcification of bone, cardiac arrhythmia, and liver and kidney damage.
- The OSHA Permissible Exposure Limit for hydrogen fluoride is 3 ppm. The American Conference of Governmental Industrial Hygienists recommends a ceiling (instantaneous) limit of 2 ppm and an 8-hour limit of 0.5 ppm.

**HF Exposure Prevention**
- HF and HF containing solutions must only be used in the Acid Hoods while wearing the full acid chemical protection gear as described in Section 6.5.6.
- Using safe practices to prevent exposure to HF are of utmost importance. Be absolutely certain that you don’t get it on you by being very careful and wearing full chemical protection gear.
- HF etches silicon dioxide very well. Therefore, it also etches glass. It must not be kept in a glass bottle, used in a glass beaker or disposed in a glass waste bottle. Plastic lab-ware is available for this purpose.

**HF First Aid and Medical Treatment**
Simple washing of an HF splash is not sufficient to prevent damage. If you suspect you have been exposed to HF, you should immediately do the following:
1. Rinse off the exposed area with water (e.g., the safety shower)
2. Immediately apply Calcium Gluconate Gel to the exposed area
3. Call 911 and request immediate medical assistance. Be sure that medical personnel know that it is an HF burn and know that it requires specific treatment different from a common acid burn.

Complete First Aid Guidelines for Treating HF exposures can be found as an Appendix to this manual, and printed copies are available at all SMIF Acid Hoods and the SMIF Emergency Response Station.
7.6.3 Piranha

Liquid **piranha** is a common name applied to a mixture of Hydrogen Peroxide and Sulfuric Acid. It is extremely aggressive toward carbonaceous materials (e.g. flesh and photoresist residue, equally). It also removes heavy metal contamination. It is used by some users for cleaning wafers. Piranha solutions are only to be used in the Acid Hoods while wearing the full acid chemical protection gear as described in Section 6.5.6.

Ensure that the used Piranha solution has stopped “fizzing” before pouring the waste into the acid hood drain. Piranha solution must never be stored, so make only the amount you need.

7.6.4 Chlorinated Solvents

Chlorinated solvents (e.g., chlorobenzene, trichloroethylene, and methylene chloride) are used in various resist processes. They are particularly bad for you, causing cancer, organ damage, etc. They should not be mixed with normal solvents in waste bottles. There are separate waste bottles for chlorinated solvents. As with most solvents, they can be readily absorbed through the skin. Chlorinated solvents also typically penetrate laboratory gloves easily. For example, trichloroethylene (TCE) will penetrate a nitrile glove in less than 5 minutes. As such, users of chlorinated solvents should take extra caution when handling these chemicals, and should double glove (wear two pairs of the nitrile lab gloves).

7.6.5 Photoresists (Glycol Ethers)

Commercial photoresists and electron beam resists are dispersed in a variety of solvents. The composition of these mixtures is generally not disclosed on the bottle; you must look on the SDS for it. One family of chemicals, the **glycol ethers**, commonly used in photoresists, masquerades under a variety of names. Members of this family of chemicals have been shown to be teratogens and have other effects on reproduction in laboratory animals. A number of recent studies have found evidence that these chemicals can lead to miscarriage and other reproductive effects.

The liquid and vapor are eye and respiratory tract irritants and may cause kidney damage, narcosis, and paralysis (in simple terms, it damages your kidneys, eyes, lungs and brains). Primary routes of exposure are inhalation, skin absorption, and skin and eye contact with vapors.

As with all chemicals, these are only the effects we know about. These experimental laboratory exposures were large amounts but nonetheless it is prudent to be careful with these solvents. **Don’t be sloppy with photoresist.** If being used properly, you should not be able to smell the photoresist.
7.6.6 Peroxides

All peroxides are highly oxidizing materials. Considerable energy can be released in their reactions with common materials. Some peroxide compounds are unstable, and can explode. We have hydrogen peroxide in the facility. Extreme care should be used in mixing solutions containing peroxides. Peroxides are incompatible with all forms of organic solvents and flammable materials.

7.6.7 Highly Toxic Compounds used in EM Sample Preparation

Chemical compounds used commonly in sample preparation for electron microscopy can be highly toxic, and should only be used in the proper chemical hood with the appropriate personal protective gear.

- **Osmium Tetroxide** affects the central nervous system, eyes, male reproductive system, and kidneys
- **Sodium Cacodylate** is a known carcinogen (contains arsenic) and can also affect the kidneys, GI tract, heart, brain, skin, bone marrow, nerves, and liver
- **Uranyl Acetate** is highly toxic and radioactive
- **Propylene Oxide** is a potential carcinogen, and can affect the reproductive system and damage DNA and chromosomes. It also affects the skin, eyes, and respiration system.
- **Lead Citrate** affects the reproductive system (fertility or an unborn child) and may cause damage to organs

7.6.8 Nanomaterials and Powders

**Powders of any kind are NOT allowed inside the SMIF cleanroom.**

Users wanting to characterize powder or nanomaterials in the SMIF facility (outside of the cleanroom) must review the appropriate information sheets supplied by Duke University’s Occupational and Environmental Safety Office below:

- [Working Safely With Toxic Powders](#)
- [Working Safely With Nanomaterials](#)

These information sheets are also posted in the individual SMIF characterization labs.
7.7 Chemical Waste

All chemical waste must be poured into the designated drain or container
All chemical waste must be poured into the designated drain or container. All chemical waste is to be collected and neutralized or consolidated, bottled and sent out as regulated chemical waste. Waste bottles are collected by the Duke OESO, repackaged, and taken away by a licensed waste hauler. The waste is burned, neutralized, or buried in licensed facilities, in accordance with EPA rules.

Each chemical hood has a drain or container for disposing of the chemicals that are allowed in that hood:

- Acid and developer hoods: Use the acid waste drains. This waste is collected in the acid waste neutralization system located in the basement.
- Solvent hoods:
  - Non chlorinated solvents: Use the solvent waste drain. This waste is collected in containers below the hood. Full containers are taken by SMIF staff and transferred to an OESO solvent waste container and ten taken to an OESO collection point.
  - Chlorinated solvents (any solvent with the word “cholor” in its name): Use the designated waste container located in the hood. Full containers are collected by SMIF staff and taken to an OESO collection point.
  - Acetic acid containing chemicals: Use the designated waste container located in the solvent hood.
- Spin Coat hoods: Solvents are collected the same as solvent hoods. However, photoresist and other spin on organics should never be poured down the waste drain, but rather collected in a designated container.

Solid materials that are contaminated with chemical waste (such as aluminum foil, wipes, dispensers, etc.) should be packed into a zip lock bag and properly labeled with the type of waste, your name, and date. The waste bag should be completely sealed. Waste bags containing solvent waste are placed in the designated contaminated solvent waste container. Waste bags containing acid waste should be left in the back corner of the acid hoods. SMIF staff will regularly pick up the chemical waste bags for transport to OESO for proper disposal. Chemical waste bags should never be placed in a regular trash container.

Waste containers must be used properly and NOT overfilled.

Disposal of chemical waste is expensive. Generally, it costs 5 to 10 times the original cost of the chemical to dispose of the waste. Please minimize your chemical waste by minimizing both your purchases and your usage. With your help we can minimize the number of waste bottles sitting around, minimize the cost, and minimize the damage to the environment all at the same time.
8.0 Gas Safety

The gases used within the facility are generally supplied under high pressure from steel compressed gas cylinders. In many cases, these cylinders are housed in special gas cabinets and fitted with a variety of high purity valves, regulators and flow control devices. Gas cylinders must be treated with respect in all cases. An enormous amount of energy is stored in the compressed gas. **Gas bottles are to be securely chained or strapped at all times.** In addition, many of these gases are toxic, or at least severely corrosive. Finally, improper use of gas cylinders and valves can result in contaminated gas and ruined samples and equipment.

**Compressed gas equipment in the facility is not user serviceable. Gas bottles are to be changed only by the appropriate staff members.**

8.1 Hazardous Gases Used

8.1.1 Pyrophoric Gases

Pyrophoric gases are defined as gases that will ignite spontaneously in air at temperatures of 130 F or below. **Silane** ($\text{SiH}_4$), which is used for the deposition of CVD silicon nitride and silicon dioxide, is an example of a pyrophoric gas. It spontaneously ignites in air at concentrations between 4 % and approximately 90 %.

8.1.2 Corrosive Gases

Corrosive gases used in the SMIF facility include the chlorine-based gases, **Chlorine** ($\text{Cl}_2$), **Boron Trichloride** ($\text{BCl}_3$), and **Silicon Tetrachloride** ($\text{SiCl}_4$). These gases are used in reactive ion etch systems and are confined in exhausted cabinets.

Chlorine is severely corrosive and is choking to breathe. Chlorine forms HCl in the lungs, causing severe tissue damage that can be fatal. As with many other corrosive gases, the effects of exposure may not be noticed for a few days. In all cases, medical attention should be sought immediately following exposure, not at the onset of symptoms.

Because of the small amounts used, the ventilation used, and the low odor threshold for chlorine exposure, accidental chlorine gas exposure is not considered a significant risk.

8.1.3 Flammable Gases

Flammable gases used in the SMIF facility include **Hydrogen** ($\text{H}_2$) and **Methane** ($\text{CH}_4$). These gases are used in reactive ion etch and/or annealing systems and are confined in exhausted cabinets.
8.1.4 Cryogenic Gases (Liquid Nitrogen)

Most people do not think of Nitrogen as a hazardous gas. However, excessive amounts of Nitrogen released into a confined space can quickly produce an oxygen deficient environment. More people die of asphyxiation by nitrogen than by any of the “toxic” gases discussed here.

We use liquid nitrogen for many things in the laboratory. Liquid nitrogen dewars are used to fill cold traps for some of the analytical equipment, and the boil off from a large tank is used for the supply of “house” nitrogen in the clean room.

8.1.5 Highly Toxic Gases

SMIF does not currently house any highly toxic gases. Examples of highly toxic gases used in the semiconductor industry include phosphine and arsine.

9.0 X-Ray Safety

All X-ray generating SMIF equipment are equipped with safety interlocks that prevent X-Ray exposure during operation. Users should never attempt to defeat these interlocks or perform maintenance or repair of this equipment. X-Ray based instruments use in SMIF are:

- Micro CT
- Small Angle X-Ray Scattering (SAXS1 and SAXS2)
- X-Ray Diffractometer (XDIF1)
- X-Ray Photospectrometer (XPS1)

10.0 Fire Safety

You will be shown the locations of all emergency exits as well as the fire pull alarms when you use the clean room or characterization labs for the first time.

In the event of fire, follow the posted Duke fire emergency procedures (RACE):

- R = Remove all persons in immediate danger
- A = Activate manual fire pull alarm and dial 911
- C = Close doors to prevent spread of fire
- E = Evacuate (only emergency personnel should attempt to extinguish a fire in SMIF due to the presence of various flammable gasses and chemicals)
This booklet describes the special First Aid and Medical Treatment measures necessary following exposure to or injury from HYDROFLUORIC ACID (HF).

However, it must be emphasized that PREVENTION of exposure or injury must be the primary goal.

Preventive measures include:
1. Making everyone who handles or uses HF aware of its properties and dangers.
2. Training everyone who uses HF in proper handling and safety precautions.
3. Utilizing all appropriate engineering controls, and making sure that the controls are maintained and functioning properly.
4. Requiring everyone who handles or uses HF to have available the proper safety and personal protective equipment, to be trained to use the equipment, and to always use the equipment when necessary.
5. Arranging ahead of time to provide first aid or medical treatment measures if necessary.

If you have questions, comments or suggestions, please write to:

Technical Service Manager - Hydrofluoric Acid
Honeywell Performance Materials and Technologies
101 Columbia Road
Montclair, New Jersey 07042-1053
NOTE: In addition to the usual medical history, the physician should obtain the following information: concentration of HF, date and time of exposure, duration of exposure, how exposure occurred, body parts exposed/affected, first aid measures instituted (what, when, how long). Injuries due to dilute HF solutions or low concentrations of vapors may result in delays in clinical presentation up to 24 hours following exposure.

1. This is a brief summary of First Aid and Medical Treatment measures. The text of the brochure “RECOMMENDED MEDICAL TREATMENT FOR HYDROFLUORIC ACID EXPOSURE” must be consulted for more complete information.

2. 2.5% - 5% calcium gluconate injections must be used if the soaks or gel do not significantly relieve pain in 30-40 minutes. Injections may also be used as the primary treatment, especially for larger and/or deeper burns.

3. Systemic effects include hypocalcemia, hypomagnesemia, hyperkalemia, cardiac arrhythmias, respiratory distress, bronchospasm, respiratory alkalosis, acidosis, and pulmonary edema. TREATMENT includes cardiac monitoring, monitoring serum calcium, fluoride, magnesium, and electrolytes, administration of N calcium gluconate, correcting magnesium and electrolyte imbalances, and, in extreme cases, hemodialysis.

4. Calcium gluconate is normally supplied in ampules containing 10% calcium gluconate. Concentrations less than 10% are obtained by diluting with normal saline.

5. Benzalkonium chloride is a high molecular weight quaternary ammonium compound available as Zephiran® a Registered Trademark of Sanofi Pharmaceuticals, New York, N.Y. 10016.

6. Registered trademark, Johnson & Johnson - Merck, Fort Washington, PA 19034

For additional reference charts or information on properties, storage and handling, or medical treatment for hydrofluoric acid, contact:

Honeywell Performance Materials and Technologies
101 Columbia Road
Morristown, N.J. 07962

In the event of a medical emergency with this product, call the 24-hour Honeywell emergency telephone number: 800-498-5701

This foldout chart is also available as a laminated 15” x 23” wall poster.
DISCLAIMER: All statements, information, and data given herein are believed to be accurate and reliable but are presented without warranty, warranty, or responsibility of any kind, express or implied. Statements or suggestions concerning possible use of our products are made without representation or warranty that any such use is free of patent infringement and are not recommendations to infringe any patent. The user should not assume that all medical and first aid measures are indicated or that other measures may not be required.

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This booklet describes the special First Aid and Medical Treatment measures necessary following exposure to or injury from HYDROFLUORIC ACID (HF).

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5. Arranging ahead of time to provide first aid or medical treatment measures if necessary.

If you have questions, comments or suggestions, please write to:

Technical Service Manager - Hydrofluoric Acid
Honeywell Performance Materials and Technologies
101 Columbia Road
Montgomery, New Jersey 07862-1053

For additional assistance, including technical information covering all aspects of hydrofluoric acid, safe handling, use and disposal write:

Honeywell Performance Materials and Technologies
Fluorine Products
101 Columbia Road
Montgomery, NJ 07862-1053

In the event of a medical emergency with this product, call the 24-Hour Honeywell emergency telephone number: 866-686-3701

To place an order, obtain prices or product availability information, call toll-free:

Within the continental United States
800-523-9000
973-455-6300

Fires in any location in Canada
888-523-9760

Recommended Medical Treatment for Hydrofluoric Acid Exposure

Hydrofluoric Acid Treatment
Quick Reference Chart
TREATMENT OF HYDROFLUORIC ACID (HF) EXPOSURE

Quick Reference

NOTE: In addition to the usual medical history, the physician should obtain the following information: concentration of HF, date and time of exposure, duration of exposure, how exposure occurred, body parts exposed/affected, first aid measures instituted (what, when, how long). Injuries due to dilute HF solutions or low concentrations of vapors may result in delays in clinical presentation up to 24 hours following exposure.

SKIN BURNS

**FIRST AID**

<table>
<thead>
<tr>
<th>CONCENTRATED HF</th>
<th>DILUTE HF</th>
<th>ALL HF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water Wash</td>
<td>Water Wash</td>
<td>Water Wash</td>
</tr>
<tr>
<td>Iced Benzalkonium Chloride* 0.13% Soaks OR Calcium Gluconate 2.5% Gel</td>
<td></td>
<td></td>
</tr>
<tr>
<td>THEN</td>
<td>Iced Benzalkonium Chloride* 0.13% Soaks OR Calcium Gluconate 2.5% Gel</td>
<td></td>
</tr>
<tr>
<td>THEN</td>
<td>Saline Wash</td>
<td></td>
</tr>
<tr>
<td>ALL HF</td>
<td>CONCENTRATED HF</td>
<td></td>
</tr>
<tr>
<td>Water Wash</td>
<td>Oxygen THEN</td>
<td></td>
</tr>
<tr>
<td>Saline Wash</td>
<td>2.5% Calcium Gluconate¹ by Nebulizer</td>
<td></td>
</tr>
<tr>
<td>(Mild Exposures)</td>
<td>DILUTE HF</td>
<td></td>
</tr>
<tr>
<td>Water Wash</td>
<td>Oxygen THEN</td>
<td></td>
</tr>
<tr>
<td>Saline Wash</td>
<td>Consider 2.5% Calcium Gluconate¹ by Nebulizer</td>
<td></td>
</tr>
<tr>
<td>ALL HF</td>
<td>DO NOT INDUCE VOMITING</td>
<td></td>
</tr>
<tr>
<td>Milk or Water</td>
<td>Milk of Magnesia OR Any Calcium Containing Antacid</td>
<td></td>
</tr>
</tbody>
</table>

**MEDICAL TREATMENT**

<table>
<thead>
<tr>
<th>CONCENTRATED HF</th>
<th>DILUTE HF</th>
<th>ALL HF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Debride (if necessary)</td>
<td>Continue Soaks OR Calcium Gluconate 2.5% - 5% Injection¹ AND Observe/forTreat Systemic Effects² (especially if &gt; 25 sq. in.)</td>
<td></td>
</tr>
<tr>
<td>DILUTE HF</td>
<td>Topical Tetracaine Hydrochloride THEN</td>
<td>Continue Calcium Gluconate by Nebulizer</td>
</tr>
<tr>
<td>Debride (if necessary)</td>
<td>Continue Soaks OR Calcium Gluconate 2.5% Gel</td>
<td></td>
</tr>
<tr>
<td>Calcium Gluconate 2.5% - 5% Injection¹ AND Observe/forTreat Systemic Effects² Unlikely</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ALL HF</td>
<td>CONCENTRATED HF</td>
<td></td>
</tr>
<tr>
<td>Continue Calcium Gluconate by Nebulizer</td>
<td>Observe and Treat for Respiratory Distress, Bronchospasm, Pulmonary Edema, Systemic Effects¹ (Inhaled Steroids and/or Bronchodilators as Needed)</td>
<td></td>
</tr>
<tr>
<td>DILUTE HF</td>
<td>Continue Calcium by Gluconate Nebulizer</td>
<td></td>
</tr>
<tr>
<td>Observe</td>
<td>Serious Effects Unlikely OR Inhalation of HF Fumes from Diluted Acid Uncommon</td>
<td></td>
</tr>
<tr>
<td>ALL HF</td>
<td>CONCENTRATED HF</td>
<td></td>
</tr>
<tr>
<td>Continue Calcium Gluconate by Nebulizer</td>
<td>Oxygen AND 2.5% Calcium Gluconate 4 by Nebulizer</td>
<td></td>
</tr>
<tr>
<td>DILUTE HF</td>
<td>Oxygen</td>
<td></td>
</tr>
<tr>
<td>THEN</td>
<td>Consider 2.5% Calcium Gluconate¹ by Nebulizer</td>
<td></td>
</tr>
<tr>
<td>ALL HF</td>
<td>DO NOT INDUCE VOMITING</td>
<td></td>
</tr>
<tr>
<td>Milk or Water</td>
<td>Milk of Magnesia OR Any Calcium Containing Antacid</td>
<td></td>
</tr>
</tbody>
</table>

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2. 2.5% - 5% calcium gluconate injection must be used if the soaks or gel do not significantly relieve pain in 30-40 minutes. Injections may also be used as the primary treatment, especially for larger and/or deeper burns.
3. Systemic effects include hypocalcemia, hypomagnesemia, hyperkalemia, cardiac arrhythmias, metabolic acidosis, and/or altered coagulation studies. TREATMENT includes cardiac monitoring, monitoring serum calcium, fluoride, magnesium, and electrolytes; administration of N calcium gluconate, correcting magnesemia and electrolyte imbalances, and in extreme cases, hemodialysis.

For additional reference charts or information on properties, storage and handling, or medical treatment for hydrofluoric acid contact:
Honeywell Performance Materials and Technologies
101 Columbus Road
Morristown, NJ 07962
In the event of a medical emergency with this product, call the 24-hour Honeywell emergency telephone number: 800-498-5701

1. Registered trademark, control C, inc; Made in the USA. 2. Registered trademark, Johnson & Johnson- Merck, Fort Washington, PA 19034

* Benzalkonium chloride is a high molecular weight quaternary ammonium compound available as Zephiran® a Registered Trademark of Sanofi Pharmaceutica, New York, NY 10016

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**WARNING:** BURNS WITH CONCENTRATED HF ARE USUALLY VERY SERIOUS, WITH THE POTENTIAL FOR SIGNIFICANT COMPLICATIONS DUE TO FLUORIDE TOXICITY. CONCENTRATED HF, LIQUID OR VAPOR MAY CAUSE SEVERE BURNS, METABOLIC IMBALANCES, PULMONARY EDEMA AND LIFE THREATENING CARDIAC ARRHYTHMIAS. EVEN MODERATE EXPOSURES TO CONCENTRATED HF MAY RAPIDLY PROGRESS TO FATALITY IF LEFT UNTREATED.
Introduction

Because the medical treatment of hydrofluoric acid exposure is so specialized and differs from the treatment of other inorganic acid exposures, physicians may be unaware of appropriate treatment measures. It is recommended that HF users ensure ahead of time that their local medical resources are familiar with the toxicity of HF and the treatment of HF exposure. This would include, at a minimum, thoroughly reviewing this booklet and making sure that treatment facilities and supplies are available.

Hydrofluoric acid (CAS # 7664-39-3) is very aggressive physiologically because of the fluoride ion. Both anhydrous hydrofluoric acid (hydrogen fluoride) and its solutions are clear, colorless liquids. When exposed to air, concentrated solutions and anhydrous hydrofluoric acid produce pungent fumes which are especially dangerous.Unless heated, dilute concentrations of hydrofluoric acid in water (e.g., less than 40% HF) do not produce significant vapor concentrations.

NOTE: Persons unfamiliar with hydrofluoric acid often mistake it for, or confuse it with, hydrochloric acid. Although hydrofluoric acid (HF) and hydrochloric acid (HCl) have similar sounding names, the toxicity of these two acids is very different. To decrease or avoid confusion, we recommend that HYDROFLUORIC ACID and HYDROGEN FLUORIDE be referred to as “HF”.

HF is primarily an industrial raw material. It is used in fluorocarbon production, stainless steel manufacturing, metal finishing, aluminum manufacturing, inorganic and organic chemical manufacturing, petroleum refining, mineral processing, glassmaking and electronic components manufacturing. It is also used in certain industrial and consumer cleaning compounds. However, its use in consumer products is discouraged because of its potential toxicity.

Most non-industrial burns are caused by dilute concentrations of HF (e.g., less than 15% HF). Most of the HF used in the electronics industry is less than 50%. However, many industrial uses of HF involve concentrated (50-100%) HF.

WARNING: BURNS WITH CONCENTRATED HF ARE USUALLY VERY SERIOUS, WITH THE POTENTIAL FOR SIGNIFICANT COMPLICATIONS DUE TO FLUORIDE TOXICITY. CONCENTRATED HF, LIQUID OR VAPOR, MAY CAUSE SEVERE BURNS, METABOLIC IMBALANCES, PULMONARY EDEMA AND LIFE THREATENING CARDIAC ARRYTHMIAS. EVEN MODERATE EXPOSURES TO CONCENTRATED HF MAY RAPIDLY PROGRESS TO FATALITY IF LEFT UNTREATED.

The recommended medical procedures described in this brochure are based on a review of the available literature, shared experiences with others who have dealt with the health effects of HF, the personal knowledge and experiences of Honeywell physicians, nurses and other professionals in dealing with the unique hazards of this product, and experimental laboratory work sponsored by Honeywell.

Every effort must be made to prevent exposure to HF. If exposure does occur, the specialized procedures which follow are recommended to avoid the very serious consequences that might otherwise occur.

Acute Toxicity

SKIN CONTACT

HF can cause serious, painful burns of the skin. Specialized first aid and medical treatment is required. Burns larger than 25 square inches (160 square cm) may result in serious systemic toxicity.

HF is a highly corrosive acid which can severely burn skin, eyes, and mucous membranes. The vapors from anhydrous hydrofluoric acid or its concentrated solutions can also burn these tissues.

HF is similar to other acids in that the initial extent of a burn depends on the concentration, the temperature, the duration of contact with the acid and the size of the burn. Hydrofluoric acid differs, however, from other acids because the fluoride ion readily penetrates the skin, causing destruction of deep tissue layers. Unlike other acids which are rapidly neutralized, this process may continue for days if left untreated.

Strong acid concentrations (over 50%), and particularly anhydrous HF (AHF or 100% HF), cause immediate, severe, burning pain and a whitish discoloration of the skin often followed by blister formation. Skin exposure to HF vapors can result in similar burns.

HF skin burns are usually accompanied by severe, throbbing pain which is thought to be due to irritation of nerve endings by increased levels of potassium ions entering the extracellular space to compensate for the reduced levels of calcium ions, which have been bound to the fluoride. Relief of pain is an important guide to the success of treatment.

The usual initial signs of an HF burn are redness, edema, and blistering. With more concentrated acids, a blanched white
area appears. The fluoride ion penetrates the upper layers of the skin. A thick granular exudate may form under blisters due to liquefaction necrosis. In rare (and untreated) cases, there may be penetration to underlying bone with decalcification. HF burns require immediate and specialized first aid and medical treatment (2, 3, 4, 5, 6, 7) differing from the treatment of other chemical burns. If untreated or if improperly treated, permanent damage, disability or death may result. (8) If, however, the burns are promptly and properly recognized and managed, the results of treatment are generally favorable.

Treatment is directed toward binding the fluoride ions to prevent tissue destruction. High molecular weight quaternary ammonium compounds, e.g. benzalkonium chloride (Zephiran®), are used as soaking agents. (9, 10, 11) Calcium gluconate as a gel or ointment can be applied locally, and calcium gluconate solution may be injected (subcutaneously, intravenously, or intra-arterially), inhaled, or used as an irritant. (3, 12, 13, 14, 15)

**Speed is of the essence.** Delays in first aid care or medical treatment or improper medical treatment will likely result in greater damage or may, in some cases, result in a fatal outcome. **During transportation to a medical facility or while waiting for a physician to see the victim, it is extremely important to continue the benzalkonium chloride (Zephiran) soaks or compresses or continue massaging calcium gluconate gel.** In contrast to the immediate effects of concentrated HF, the effects of contact with more dilute hydrofluoric acid or its vapors may be delayed, and this is one of the problems with the recognition of some HF burns. Skin contact with acid concentrations in the 20% to 50% range may not produce clinical signs or symptoms for one to eight hours. With concentrations less than 20%, the latent period may be up to twenty-four hours. HF concentrations as low as 2% may cause symptoms if the skin contact time is long enough. (1)

**SYSTEMIC TOXICITY**

To produce HF, calcium fluoride is reacted with sulfuric acid:

\[
\text{CaF}_2 + \text{H}_2\text{SO}_4 \rightarrow 2\text{HF} + \text{CaSO}_4
\]

This production process requires a great deal of energy to accomplish. On the other hand, in the body:

\[
2\text{HF} + \text{Ca}^{++} \rightarrow \text{CaF}_2
\]

This process releases energy, and therefore occurs very readily. The toxic effect of HF on body calcium is certainly more complicated than this. There is some evidence that fluoride may combine with calcium and phosphate, so that five calcium ions are tied up for each fluoride ion (e.g. \(\text{Ca}_5\text{F} (\text{PO}_4)_3\)), rather than two. There is also some evidence that there may be high intracellular levels of calcium in some tissues, rather than low levels, as would intuitively be expected. (16) However, the reaction of fluoride with body calcium is one of the major toxic effects and forms the basis for many treatment recommendations.

One of the most serious consequences of severe exposure to HF by any route is the marked lowering of serum calcium (hypocalcemia) and other metabolic changes, which may result in a fatal outcome if not recognized and treated. Hypocalcemia should be considered a potential risk in all instances of inhalation or ingestion, and **whenever skin burns exceed 25 square inches**, (160 square centimeters). Serum magnesium may also be lowered, and elevations in serum potassium have been reported to further complicate the metabolic imbalances which need to be monitored and corrected. (16, 17, 18) High levels of fluorides have been noted both in the blood and body organs. Hemodialysis has been reported to be effective therapy for cases of severe systemic fluoride intoxication. (19, 20, 21) Treatment for shock may also be required as for other severe injuries.

Other effects reported from fluoride exposure include coagulation defects and inhibition of a number of enzymes, including preglycolytic enzymes, phosphatases and cholinesterase. The results of this enzyme inhibition include inhibition of cellular glucose phosphorylation and subsequent glycolysis, inhibition of respiration, and increased sensitivity of cholinergic mechanisms to acetyl cholinesterase. (22)

While hypocalcemia has been traditionally considered the major systemic effect of severe poisoning with HF, it is apparent that hypomagnesemia, hyperkalemia, the cardiodepressing and vasodilating effects of fluoride and effects on pulmonary hemodynamics and systemic capacitance vessels, including an increase in pulmonary vascular resistance, all play a role in systemic toxicity. Although some of these effects have been described, the implications for therapeutic measures have not been well defined. (23, 24)

**EYE CONTACT**

Hydrofluoric acid can cause severe eye burns with destruction or opacification of the cornea. Blindness may result from
severe or untreated exposures. Immediate first aid and specialized medical care is required. (3,13)

**INHALATION**

Hydrofluoric acid fumes may cause laryngospasm, laryngeal edema, bronchospasm and/or acute or delayed pulmonary edema. Acute symptoms may include coughing, choking, chest tightness, chills, fever and cyanosis. Many reported fatalities from HF exposures have been due to severe pulmonary edema (coupled with systemic toxicity) that did not respond to usual medical treatment.

Burns from vapors or liquid contact to the oropharyngeal mucosa or upper airway may cause severe swelling to the point of requiring a tracheostomy. It is recommended that all patients with such exposures be hospitalized for observation and/or treatment.

Because of the strong irritant nature of HF, an individual inhaling HF vapors or fumes will usually experience upper respiratory injury, with mucous membrane irritation and inflammation as well as cough. All individuals suspected of having inhaled HF should be observed for pulmonary effects. This would include those individuals with significant upper respiratory irritation, bronchoconstriction by pulmonary auscultation or spirometry, and any individual with HF exposure to the head, chest or neck areas. It has been reported that pulmonary edema may be delayed for several hours and even up to two days. If there is no initial upper respiratory irritation, significant inhalation exposure can generally be ruled out.

The Permissible Exposure Limit (PEL) set by the U.S. Occupational Safety and Health Administration (OSHA) is a time weighted average exposure for 8 hours of 3 ppm. (25) The American Conference of Governmental Industrial Hygienists (ACGIH) recommends a ceiling level of 2 ppm or 1.53 mg/m³ with a 0.5 ppm TLV-TWA. (26) The National Institute for Occupational Safety and Health (NIOSH) has established the level that is immediately dangerous to life and health (IDLH) at 30 ppm. (27, 28) The American Industrial Hygiene Association has published an Emergency Response Planning Guideline setting 50 ppm as the maximum level below which nearly all individuals could be exposed for one hour without experiencing or developing life-threatening health effects (ERPG-3), 20 ppm as the maximum level below which nearly all individuals could be exposed for one hour without developing irreversible health effects or symptoms which would impair taking protective action (ERPG-2), and 2 ppm as the maximum level below which nearly all individuals could be exposed up to one hour without experiencing other than mild, transient adverse health effects (ERPG-1). (29)

The California Occupational Safety and Health Standards Board has established a PEL of 0.4 ppm 8hr TWA \[0.33\text{mg/m}^3\] with a STEL (Short term exposure level) of 1 ppm [0.83mg/m³]. (32)

**INGESTION**

Ingestion of HF may result in severe burns to the mouth, esophagus and stomach. Severe systemic effects are common. Ingestion of even small amounts of dilute HF have resulted in death. (30)

Toxic myocarditis, believed to be associated with HF Acid ingestion with a suicide attempt has been reported. (5)

**Chronic Toxicity**

Because it is a strong irritant there are few exposures to HF sufficient to suggest risk of chronic toxicity. HF has not been the subject of long term toxicity studies or testing. Once HF enters the body, it is expected that the fluoride ion would be the major concern from a chronic toxicity standpoint. Chronic toxicity from long term, high exposure to fluoride salts (eg. SnF₂, NaF, Na₂FPO₃) has been reported to result in tooth mottling in children, bone fluorosis and sometimes osteosclerosis in adults and children.

Skeletal fluorosis is known to be associated with excessive exposure to fluoride compounds. Cases of skeletal fluorosis have been reported in populations exposed to naturally occurring drinking water containing greater than 10 ppm of fluoride ion and in individuals exposed to high levels of fluoride containing dusts. However, skeletal fluorosis has not been reported as a consequence of HF exposure.

Because of the use of fluoride to prevent dental caries, there is ongoing evaluation of fluorides for the potential to cause cancer. There is no evidence that fluoride is genotoxic except in some in vitro assays at cytotoxic concentrations. Epidemiological studies have not demonstrated an association between fluoride in drinking water and an increase in cancer. The International Agency for Research on Cancer (IARC) has not classified hydrogen fluoride as to its human carcinogenicity, and neither fluorides nor HF are listed by IARC, NTP, OSHA, ACGIH, NIOSH, the State of California or
other governmental agencies as causing cancer. (31, 32, 33) In animal studies, fluoride salts have caused effects in offspring only at high, maternally toxic levels. Some animal studies have shown effects on male fertility, e.g., decreased sperm counts. (33) Fluoride exposures should be kept below recommended levels to assure no adverse effects to the developing fetal skeletal system or teeth.

Monitoring of urine for fluorides is an accepted method of determining exposure. (34) Urine fluoride levels above 3 mg/liter at the beginning of a workshift, or above 10 mg/liter at the end of a workshift, may indicate excessive absorption of fluoride. It should be noted that fluorides are often present in significant amounts in persons not occupationally exposed (because of dietary sources of fluoride such as tea), and that the urine fluoride determination is not specific for HF. (26)

First Aid Treatment for Hydrofluoric Acid Burns

In Case of Contact or Suspected Contact with HF:

**SKIN CONTACT**

1. Move victim immediately under safety shower or other water source and flush affected area thoroughly with large amounts of running water. Speed and thoroughness in washing off the acid is of primary importance.

2. Begin flushing even before removing clothing. Remove all contaminated clothing while continuing to flush with water.

3. Rinse with large amounts of running water. If 0.13% benzalkonium chloride (Zephiran) solution or 2.5% calcium gluconate gel are available, the rinsing may be limited to 5 minutes, with the soaks or gel applied as soon as the rinsing is stopped. If benzalkonium chloride (Zephiran) or calcium gluconate gel is not available, rinsing must continue until medical treatment is rendered.

4. While the victim is being rinsed with water, someone should alert first aid or medical personnel and arrange for subsequent treatment.

5. Immediately after thorough washing, use one of the measures below:

   a. Begin soaking the affected areas in iced 0.13% benzalkonium chloride (Zephiran) solution.

Use ice cubes, not shaved ice, in order to prevent frostbite.

If immersion is not practical, towels should be soaked with iced 0.13% benzalkonium chloride (Zephiran) solution and used as compresses for the burned area. Compresses should be changed every two to four minutes. Do not use benzalkonium chloride (Zephiran) solution for burns of the eyes. Exercise caution when using benzalkonium chloride (Zephiran) solution near the eyes as it is an eye irritant. Benzalkonium chloride (Zephiran) soaks or compresses should be continued until pain is relieved or until more definitive medical treatment is provided.

   b. Start massaging 2.5% calcium gluconate gel into the burn site.

Apply gel frequently and massage continuously until pain and/or redness disappear or until more definitive medical care is given.

The individual applying the calcium gluconate gel should wear surgical gloves to prevent a possible secondary HF burn.

   **NOTE:** Clinical experience has shown that both benzalkonium chloride (Zephiran) and calcium gluconate gel are effective when used correctly in appropriate situations. In an animal model, benzalkonium chloride (Zephiran) soaks are superior to calcium gluconate gel under the experimental conditions used. (37, 38)

6. After treatment of burned areas is begun, the victim should be examined to ensure there are no other burn sites which have been overlooked.

7. Arrange to have the victim seen by a physician. (If burns are small and/or caused by weak acid, and treatment has been provided by an experienced individual, evaluation by a physician may not be necessary.) During transportation to a medical facility or while waiting for a physician to see the victim, it is extremely important to continue the benzalkonium chloride (Zephiran) soaks or compresses or continue massaging calcium gluconate gel. In many situations, particularly for minor burns covering a small skin area or for burns caused by dilute HF, continued treatment with soaks or gel may be effective as the sole type of medical care. All persons with extensive burns or burns with significant blister formation or with the appearance of whitish or dead
skin need to be seen by a physician. All persons with HF burns which do not respond to either calcium gluconate gel or benzalkonium chloride (Zephiran) soaks or compresses within 30 minutes should be evaluated by a physician.

8. The physician may advise continuation of benzalkonium chloride (Zephiran) soaks or calcium gluconate gel.

a. If the physician advises continued treatment with benzalkonium chloride (Zephiran) soaks or compresses, the soaks or compresses are usually required for 2 to 4 hours. Significant relief of pain should be noted within the first 30 minutes. If this does not occur, the victim must be seen by a physician and more definitive care instituted. If the pain is substantially relieved within the first 30 minutes, continue the treatment for a total of 2 hours. After that time, discontinue treatment and observe for the recurrence of pain. If pain recurs, continue soaks or compresses until relief of pain occurs. Soaking for 6 hours is sometimes needed. (Note: Because prolonged immersion in the ice bath may result in discomfort, relief may be obtained by removing the part from the bath every 10 minutes for a minute or so and then reimmersing it. After the initial 30-60 minutes of treatment, less ice can be used so the bath is cool rather than cold.)

b. Calcium gluconate gel may be used for several hours or even repeated over a period of a few days. However, if significant relief of pain does not occur within 30 to 40 minutes, more definitive treatment such as Calcium Gluconate injections or iced benzalkonium chloride (Zephiran) will be required. For small burns, or burns of the face, ears, and near mucous membranes, calcium gluconate gel may be very useful. The gel is applied frequently and massaged into the burned area. This is continued until relief is obtained or further medical care is available.

9. For serious burns, medical attention must be provided as quickly as possible.

For minor burns, if first aid treatment does not alleviate symptoms or if symptoms persist or recur, medical attention must be sought.

EYE CONTACT

1. Immediately flush the eyes for at least 15 minutes with large amounts of gently flowing water. Hold the eyelids open and away from the eye during irrigation to allow thorough flushing of the eyes. Do not use the benzalkonium chloride (Zephiran) solutions described for skin treatment. If the person is wearing contact lenses, the lenses should be removed, if possible. However, flushing with water should not be interrupted, and the lenses should be removed by a person who is qualified to do so. If sterile 1% calcium gluconate solution is available, water washing may be limited to 5 minutes, after which the 1% calcium gluconate solution should be used to irrigate the eye using a syringe or a continuous irrigation device.

2. Take the victim to a doctor, preferably an eye specialist, as soon as possible. Ice water compresses may be applied to the eyes while transporting the victim to the doctor.

3. If a physician is not immediately available, apply one or two drops of 0.5% tetracaine hydrochloride, 0.5% proparacaine, or other aqueous, topical ophthalmic anesthetic and continue irrigation. Use no other medications unless instructed to do so by a physician. Rubbing of the eyes is to be avoided.

INHALATION

1. Immediately move victim to fresh air and get medical attention.

2. Keep victim warm, quiet and comfortable.

3. If breathing has stopped, start artificial respiration at once.

4. 100% Oxygen should be administered as soon as possible by a trained individual. Continue oxygen while awaiting medical attention unless instructed otherwise by a physician.

5. A nebulized solution of 2.5% calcium gluconate may be administered with oxygen by inhalation.

6. Do not give stimulants unless instructed to do so by a physician.

7. The victim should be examined by a physician and held under observation for at least a 24 hour period.

INGESTION

1. Have the victim drink several large glasses of water or milk to dilute the acid. Do not induce vomiting. Do not give emetics or baking soda. Never give anything by mouth to an unconscious person.

2. Give several glasses of milk or several ounces of milk of magnesia, any calcium containing antacid®, Maalox®, etc or grind up and administer up to 30 Tums®, Caltrate® or other antacid tablets with water. The calcium or magnesium in these compounds may act as an antidote, however this has not been supported in the literature (39).
3. Get immediate medical attention. Ingestion of HF is a life-threatening emergency.

Medical Treatment for Hydrofluoric Acid Burns

BURNS OF THE SKIN – GENERAL

Burns from dilute acid are difficult to distinguish from other chemical burns and usually appear as areas of erythema. However, they may progress, if not treated, to areas of blistering, necrosis or ulceration. Burns from more concentrated acid have a characteristic appearance and present as severely reddened, swollen areas with blanched, whitish regions which rapidly progress to blistering and necrosis. A thick granular exudates usually appears under these blisters and requires debridement and removal.

Concentrated HF burns cause extreme pain. The pain is thought to result from nerve ending irritation due to increased levels of potassium ions in extracellular spaces to compensate for the reduced levels of calcium ions which have been bound by the fluoride. Relief of pain is an excellent indication of the success of treatment and, therefore, local anesthetics should be avoided.

Many different types of therapies have been suggested for HF burns. The aim of all treatment is to chemically sequester the fluoride ion and to prevent extensive, deep-tissue destruction. (37, 38)

After treatment of recognized burned areas is begun, the victim should be carefully examined to insure there are no other burn sites which may have been overlooked.

QUATERNARY AMMONIUM COMPOUNDS

Most HF burns can be satisfactorily treated by immersion of the burned part in an iced, aqueous solution of a quaternary ammonium compound. Two solutions have been clinically successful, 0.13% benzalkonium chloride (e.g. Zephiran) or 0.2% benzethonium chloride. Because of its availability as a non-prescription drug, benzalkonium chloride (Zephiran) is recommended in the United States.

The solutions should be cooled with ice cubes. (Shaved or crushed ice may cause excessive cooling, with the danger of frostbite.) If immersion in the solution is not practical, soaked compresses of the same iced solution should be applied to the burned area. The immersion or compresses should be used for at least two hours. Compresses should be changed or soaked with additional solution approximately every two to four minutes.

If blisters are present, they should be opened and drained and necrotic tissue should be debrided by a physician or qualified health care practitioner as soon as possible. However, immersion in benzalkonium chloride (Zephiran) or use of compresses should not be delayed if debridement cannot be accomplished immediately.

Prolonged immersion in the iced benzalkonium chloride (Zephiran) bath may result in discomfort due to excess chilling; relief may be obtained by removing the burned part from the bath every ten to fifteen minutes for a few minutes and then reimmersing it when pain recurs. After the initial 30-60 minutes of treatment, less ice can be used so the bath is cool rather than cold.

The success of this treatment is indicated by relief of the severe pain in the burned area. If there is no significant relief of pain within 30 to 40 minutes, the use of 2.5 - 5% calcium gluconate injections may be necessary. If pain recurs when the treatment is stopped at the end of the first two hours, immersion or compresses should be resumed until pain is relieved. A total of four to six hours immersion or use of compresses of benzalkonium chloride (Zephiran) may be required for the treatment of most burns. No further iced Zephiran treatment will be required in many instances. The use of iced quaternary ammonium compound solutions offers several advantages over topical calcium gluconate gel:

- ability to treat burns on multiple surfaces, such as the hand, more efficiently;
- reduction of local pain;
- possible slowing of the rate of tissue destruction;
- possible slowing of the passage of the fluoride ion into deeper tissues and into the bloodstream;
- does not require continuous massaging.

Large burns, serious burns due to concentrated HF, or burns with delayed treatment will probably require the use of calcium gluconate injections in addition to or instead of the benzalkonium chloride (Zephiran) soaks.
Quaternary ammonium compounds should not be used for burns on the face, ears or other sensitive areas due to their irritating nature. It is preferable to use calcium gluconate gel or calcium gluconate injection in these areas.

**CALCIUM GLUCONATE GEL**

Calcium gluconate gel, consisting of 2.5% USP calcium gluconate in a surgical water soluble lubricant, is widely used for first aid and/or primary treatment of HF burns of the skin. The gel is convenient to carry and can be used to initially treat small burns that might occur away from medical care. (The gel is not recommended for burns with concentrated HF except as a first aid measure.) The gel is used by massaging it promptly and repeatedly into the burned area, until pain is relieved. If possible, surgical gloves should be worn during initial application of the gel, so the person providing treatment will not receive a secondary HF burn. This treatment can be started without waiting for medical direction. Several commercially available calcium gluconate gel formulations have been evaluated and found to give comparable outcomes. (35)

If used as the only method of treatment, liberal quantities of calcium gluconate gel must be massaged into the burned area continuously for up to several hours. Relief of pain can be used to assess the efficacy of this treatment. If good relief of pain is not obtained after 30-40 minutes, alternate methods of treatment such as calcium gluconate injections or benzalkonium chloride (Zephiran) soaks should be considered.

The gel is especially useful for burns on the face, particularly near the mouth, eyes, on the ears, or for small, dilute acid burns elsewhere. It may be convenient to use the gel for very small burns where the victim can easily apply and massage the gel into the burned area. Use of the gel may be more convenient for dilute acid burns such as occur with commercial products like rust removers, aluminum cleaners or etching solutions.

**CALCIUM GLUCONATE INJECTIONS**

After first aid measures have been taken, injection of a 2.5% - 5% calcium gluconate solution is indicated as the primary medical treatment for large burns (over 25 square inches or 160 square centimeters). For smaller burns, if benzalkonium chloride (Zephiran) soaks or calcium gluconate gel do not result in significant relief of pain within 30 to 40 minutes, injection of calcium gluconate solution is indicated. Injection of calcium gluconate solution may also be indicated for burns in which treatment has been delayed.

The physician should inject sterile 2.5 - 5% aqueous calcium gluconate beneath, around and into the burned area. Calcium gluconate is packaged as a 10% solution, and must be diluted 50:50 or 25:75 with normal saline to make 5% or 2.5% solutions. (Note: DO NOT USE calcium chloride, which is corrosive and may result in additional damage.)

If subcutaneous calcium gluconate injections are used, the amount injected initially is small and should not exceed 0.5 cc per square centimeter of affected skin surface. The injections should not distort the appearance of the skin. A small-gauge needle (27-30 gauge) should be used, and the burned area should be injected through multiple sites. With successful treatment, pain relief following injection of 2.5% - 5% calcium gluconate solution is very rapid. The patient can usually advise when the pain stops, and this is an indicator of adequate treatment. Multiple injections in skin that has compromised integrity may increase the risk of infection, and the use of antibiotic creams such as Silvadene® (silver sulfadiazine) or Garamycin® (gentamicin sulfate cream) should be considered following such treatment. Local anesthetics should not be used since they mask pain relief which is an important indication of adequacy of treatment.

Some physicians prefer using calcium gluconate injections initially as the primary treatment, instead of using quaternary ammonium compound soaks or compresses or calcium gluconate gel. Injections often are not necessary when there has been early and adequate treatment with soaks or gel.

**CALCIUM GLUCONATE SOLUTION**

In some instances, a 5% or 10% calcium gluconate solution may be used in compresses or for irrigation. For example, irrigating with a calcium gluconate solution may be the best treatment should HF enter the external ear canal. In this instance, referral to an otolaryngologist may also be needed.

**BURNS OF THE FINGERS AND NAILS**

Burns of the fingers often create special problems in treatment. Finger and toe nails permit penetration of fluoride ions but prevent soaks or gels from being effective. It may be necessary to drill, split or even remove nails to allow the topical methods of treatment to be effective. One author has cautioned that removal of the nail should rarely be necessary in the case of dilute HF acid (less than 10%) burns. (40) The treating physician must consider the
morbidity associated with removal of the nail versus the need to treat the HF exposure.

If immersion in benzalkonium chloride (Zephiran) solution is started immediately, it may be possible to avoid removing the nail. Sometimes better penetration under the nail can be successfully accomplished by splitting the nail or by drilling several burr holes in the nail using a large gauge needle or a nail drill. If calcium gluconate injection is used as treatment, the nail may still need to be split or removed. If nail removal is necessary, using a short acting regional or ring-block anesthetic may facilitate this procedure and not interfere with using pain relief as an indicator of effective treatment. When using calcium gluconate injections in the digits, care must be taken to inject the solution cautiously so as to avoid compromising the circulation in these areas.

If benzalkonium chloride (Zephiran) soaks are not available, experience has shown that some finger or hand burns can be treated by using a glove filled with calcium gluconate gel. Initially, calcium gluconate gel should be massaged into the burned area. Following this, an oversize surgical glove should be partially filled with calcium gluconate gel, and the hand inserted into the glove. The gloved hand may be immersed in ice water, if available, which may aid pain relief. This treatment works best for burns where there is no blistering, or after the burns have been debrided. As in other cases where calcium gluconate gel is used, alternate methods of treatment should be considered if good relief of pain is not achieved within 30-45 minutes. If pain is relieved, the glove should remain in place for three to four hours.

**INTRA-ARTERIAL AND INTRAVENOUS CALCIUM INFUSION**

Reports in the literature have described the use of intra-arterial injection or infusion of dilute calcium gluconate solutions to treat HF burns of the hand and digits. This method, although rather involved, should be considered in selected cases, especially where inadequate or delayed treatment has occurred. The method is described as follows:

“A long catheter was inserted percutaneously into the radial artery using standard aseptic technique. Intra-arterial catheter placement was confirmed by pressure transducer and oscilloscope. If the burn involved only the thumb, index, or long fingers, the catheter was advanced only a few centimeters proximally in preparation for digital subtraction arteriography. If the burn involved the ring or small fingers, the catheter was advanced proximally into the brachial artery because access to the ulnar circulation was necessary. Following satisfactory placement of the arterial catheter, digital subtraction arteriography was performed on all patients in our series to identify the origin of vascular supply to digits involved.

Once the tip of the arterial catheter was in the desired location, a dilute preparation of calcium gluconate (10 ml of a 10% solution mixed in 40 to 50 ml 5% dextrose) was infused with a pump apparatus into the catheter over four hours. Each patient was observed closely during the infusion period for progression of symptoms and potential complications of the procedure, such as alterations of distal vascular supply.

Following the four-hour infusion, the arterial catheter was maintained in place in the usual manner while the patient underwent an observation period. If typical HF pain returned within four hours, a second calcium infusion was repeated until the patient was pain free four hours following completion of the calcium infusion.” (14)

There are now several reports of the successful use of intravenous calcium gluconate to treat HF burns of the upper extremity. (41, 42, 43) Graudins, et al. describe their method:

An intravenous catheter was placed on the dorsum of the affected hand. The superficial veins were exsanguinated by elevation. A double-cuffed pneumatic tourniquet was applied above the elbow, inflated to 100 mm Hg above systolic blood pressure, and 10 ml of 10% calcium gluconate diluted with 30 to 40 ml of 0.9% saline solution was then infused. Ischemia was maintained for 25 minutes; the cuff was sequentially released over 3 to 5 minutes. This Bier Block method was most successful for burns due to dilute acid. If the use of intravenous calcium gluconate was not successful in relieving pain (which occurred with burns due to 49% HF, the highest concentration seen in the series of patients), Graudins et al. turned to intra-arterial calcium gluconate infusion.

**ADDITIONAL MEASURES**

HF burns are very aggressive and it is extremely important that there be no delays during decontamination, first aid or medical treatment. Assuring continuous care after decontamination is critical to ensure a good result from medical treatment.
In instances of extensive burns, skin grafting has occasionally been required, but the need for this treatment should be markedly reduced by immediate and aggressive primary treatment.

Follow-up care requires monitoring to prevent secondary infections. The use of daily dressings with antibiotic creams such as Silvadene or Garamycin has proven effective. HF burns may heal slowly, but if properly treated most heal with little or no scarring in 14 to 28 days.

**ADDITIONAL AND UNPROVEN THERAPIES**

The use of intravenous calcium gluconate is discussed above. Both Williams, et al. (44) and Cox, et al. (45) have discussed the use of intravenous magnesium sulfate to treat localized moderate to serious skin burns. Using either a rat or a rabbit model, the authors administered intravenous magnesium sulfate. Cox used a 0.2 mEq bolus over two minutes, followed by a slower infusion of 0.2 mEq per hour for four hours, with a total of 1.0 mEq/kg magnesium sulfate administered. Williams administered 8 mg/kg over five minutes or 160 mg/kg over 10 minutes. These authors compare this dose to the amount of magnesium sulfate, infused more slowly, used in the treatment of eclampsia.

Dunn, et al. (37) have shown effectiveness of locally applied calcium acetate solution, 10% in water at room temperature, in an animal model.

Seyb et al. (47), performed an experiment in rats using a topically applied solution of 50% aqueous dimethyl sulfoxide (DMSO) containing calcium gluconate (20% wt/vol). This treatment gave results comparable to injecting 10% calcium gluconate or 10% magnesium sulfate, and was superior to calcium gluconate gel in treating experimental HF burns.

It should be noted that many of these therapies, while promising, have been tested to a limited degree, if at all, in humans. A product developed in France, “Hexafluorine” (46), has been marketed in Europe and the United States for use as a decontamination solution for HF skin and eye exposure. Honeywell has conducted animal studies on this product with equivocal test results. Scientific documentation of effectiveness and experience with this product are lacking at this time and we therefore do not recommend its use (48).

**SYSTEMIC ABSORPTION AND METABOLIC EFFECTS**

Significant amounts of fluoride ion may be absorbed by skin contact, inhalation, or by ingestion. If systemic absorption of fluoride occurs, hypocalcemia, hypomagnesemia and hyperkalemia may also occur. All of these parameters need to be monitored and appropriate therapeutic measures instituted. The patient should be observed for clinical signs of hypocalcemia following ingestion or inhalation or following extensive burns greater than 25 square inches. Serum calcium determinations must be performed immediately and periodically to monitor and treat hypocalcemia. Severe lowering of serum calcium levels can occur within one to two hours even with HF burns covering less than 2.5% of body surface area. (8) Continuous EKG monitoring to observe prolongation of the Q-T interval may be useful to detect early changes in serum calcium, although profound hypocalcemia following HF exposure has been reported in the absence of EKG changes or in the absence of other signs of tetany.

The fall in serum calcium may occur precipitously following HF exposure. In two reported cases of exposure to anhydrous HF, the serum calcium fell to levels around 3 milliequivalents per liter (mEq/L) [normal = 8.8 - 10.3 mEq/L] within one to three hours of exposure. (8)

If necessary, aqueous calcium gluconate may be given intravenously. Calcium gluconate as a 10% solution must be given slowly since excess calcium can produce vagal bradycardia, ventricular arrhythmias and ventricular fibrillation. The IV calcium gluconate should be repeated until serum calcium levels return to, and remain at, normal levels. In one fatal case, 280 mEq of calcium over four hours was not sufficient to correct the profound hypocalcemia. (8) Without additional measures such as hemodialysis, it may not be possible to correct extreme hypocalcemia.

Serum magnesium levels should also be monitored and magnesium loss should be replaced intravenously if indicated. Yamaura, et al. have reported a case of HF exposure in which prolonged QT interval occurred, in which ionized calcium levels were relatively high but the magnesium level was low. (49) Serum potassium must also be carefully monitored. Significant elevations of serum potassium have been noted in cases of fluoride toxicity and also in laboratory studies. Hyperkalemia has also been implicated as a causative factor in cardiovascular collapse, and should be treated appropriately.
Even with normalization of serum calcium and potassium, life threatening ventricle arrhythmia may occur, possibly due to a direct toxic effect of the fluoride ion on the myocardium. (36).

**HEMODIALYSIS** with fluoride free water (and normal to low potassium and slightly higher calcium concentrations), in conjunction with other treatments mentioned, should be considered in all cases of serious burns and may need to be repeated if indicated. (19, 20, 21) Serum fluoride levels should be monitored. Normal plasma fluoride levels may differ because of various methodologies and analytical techniques. The decision to use dialysis should be based on the HF exposure (concentration, body surface area) and the clinical condition of the patient, including the serum levels of fluoride, calcium and potassium.

*Primary excision* or surgical removal of tissue has been recommended by some practitioners as a method of reducing systemic absorption of fluoride. (50) While this could in some instances be life saving, it is a rather drastic measure. It is likely that renal dialysis could be used to effectively treat systemic toxicity and would not result in the disfigurement, disability, or morbidity which could be associated with primary excision.

**EYE INJURIES**

HF can cause severe eye burns, which, if not properly treated, may result in scarring and blindness. The prognosis is not good if first aid treatment is delayed or inadequate. After first aid treatment (see FIRST AID section) the following medical treatment may be provided:

If the individual wears contact lenses, it is usually best to remove the lenses before additional eye irrigation.

Mix 50 ml of 10% calcium gluconate with 500 ml of normal saline to give approximately a 1% calcium gluconate solution. After administering local anesthetic eye drops, use an eye clamp and IV infusion set or a two pronged nasal oxygen cannula to instill the solution over a period of one to two hours. Other irrigation devices, such as a Morgan Lens may be utilized as well. More prolonged use of the solution could possibly damage the cornea. Consult an ophthalmologist regarding additional treatment.

**INHALATION INJURIES**

Patients with inhalation exposures should also be observed for signs of systemic absorption and fluoride toxicity.

Exposure to hydrofluoric acid fumes can cause acute respiratory irritation, bronchospasm, and/or pulmonary edema. Medical personnel should also be alert to the possibility of development of pulmonary edema when extensive burns of the face, neck or chest have occurred. Intubation should be avoided, if possible.

The victim should be removed from exposure and administered 100% oxygen immediately. The use of 2.5% aqueous calcium gluconate given by nebulizer with 100% oxygen, or with intermittent positive pressure, has been recommended. Theoretically, this should reduce toxicity and damage from the fluoride ion and should be seriously considered in cases of inhalation exposure.

Repeated use of nebulized calcium gluconate, every 4 hours for 48 hours after a significant inhalation exposure, has been described. (51)

Burns of the oral mucosa or upper airway may cause severe swelling and necessitate a tracheostomy. It is, therefore, recommended that all such patients be admitted to a hospital for observation.

Because inhalation of HF may be associated with significant bronchospasm, inhaled, oral or parenteral bronchodilators should be administered as necessary. Even in the absence of symptoms, the prophylactic administration of inhalational steroids (e.g. beclomethasone dipropionate) may be indicated. (21) Pulmonary function testing may be helpful in assessing the degree and progress of pulmonary injury.

Specific measures may be needed to treat pulmonary edema.
INGESTION INJURIES

After first aid is completed (drinking several glasses of water followed by two glasses of milk or two ounces of milk of magnesia, or other calcium or magnesium containing antacids), the stomach may be lavaged with a solution of a calcium containing antacid. The Lavage tube must be passed with care to prevent perforation. Treatment for the corrosive effects is the same as for ingestion of other strong acids. Systemic toxicity is very likely to occur and may require aggressive treatment.
References

26. 2011 Threshold Limit Values (TLVs®) for Chemical Substances and Physical Agents and Biological Exposure Indices (BEIs®), American Conference of Governmental Industrial Hygienists, Inc., Cincinnati, Ohio, 2011.
32. www.dir.ca.gov/oshsb/airborn_contaminants_2011.html
Appendix

FIRST AID AND MEDICAL SUPPLIES

The following supplies should be maintained in a dispensary or first aid station near hydrofluoric acid handling and storage areas:

1. Benzalkonium chloride (Zephiran) solution*

   a. For soaks and compresses, 3 to 4 gallons of 0.13% water solution of benzalkonium chloride (Zephiran). The 0.13% solution is available as a non-prescription drug in gallon containers. The solution should be obtained in advance. It should replaced before the expiration date on the label. It is recommended that it be stored in properly labeled light-resistant containers.

   Benzalkonium chloride (Zephiran) is also available as a 17% solution. If this concentrate is used to make a 0.13% (1:750) solution, the dilution should be performed by a qualified individual, such as a registered pharmacist. The shelf life of the diluted solution is uncertain, and it should be replaced annually.

   Benzalkonium chloride (Zephiran) should be available as a non-prescription drug through most local pharmacies. The local pharmacies obtain it from pharmaceutical wholesale distributors.

   In addition to benzalkonium chloride (Zephiran), benzethonium chloride (Hyamine 1622®) has also been used successfully to treat HF burns. Because of its availability as a nonprescription drug, benzalkonium chloride (Zephiran) is recommended.

   b. Ice cubes (not crushed or shaved ice).

   c. Assorted basins (for immersing burned areas in benzalkonium chloride (Zephiran solution).

   d. Towels (for use as wet compresses).

2. Calcium gluconate gel, 2.5%

   Calcium gluconate gel is available commercially.

   It may also be made by mixing one ampule of 10% calcium gluconate solution for each ounce of a water based lubricating jelly (e.g., K-Y® Brand Lubricating Jelly) using 40 cc per 4 ounce tube. This has the advantage that the ingredients may be readily available. In addition, the ingredients may be stored separately until needed, and shelf life is less of a concern.

   In an emergency calcium gluconate gel (2.5% calcium gluconate in a water soluble base) may also be formulated by a pharmacist by dissolving 3.2 grams of calcium gluconate USP in 5 cc of sterile water, and then mixing with 120 cc (4 oz. tube) of K-Y® Jelly or other water soluble lubricant (2.5 grams per 100 cc lubricant).

3. Aqueous calcium gluconate, 10% USP, 10 cc ampules

   (4.5 mEq calcium or 93 mg elemental calcium per 10 cc)

   a. To make calcium gluconate gel, or

   b. To mix with sterile saline for eye irrigation (5 ampules 10% calcium gluconate per 500 cc sterile normal saline for a 1% solution), or

   c. To mix with sterile saline for administration with oxygen by nebulization (10 cc 10% calcium gluconate in 30 cc sterile saline for a 2.5% solution), or

   d. To be administered by a physician. When injected subcutaneously, 10% calcium gluconate must be diluted 50:50 or 25:75 with normal saline to make 5% or 2.5% solutions.

4. Sterile 0.9% saline

   a. Vials, (e.g. 10 cc, 30 cc, or 50 cc) to dilute 10% calcium gluconate to 2.5% - 5% for injection, or to 2.5% for nebulization.

   b. 500 cc IV to dilute 10% calcium gluconate to 1% for eye irrigation.

5. 0.5% tetracaine hydrochloride solution to counteract blepharospasm and facilitate eye irrigation.

6. Medical oxygen

7. Nebulizer, to administer 2.5% calcium gluconate with oxygen.

8. Beta adrenergic bronchodilators and steroids for inhalation.

9. Surgical gloves

10. Syringes and needles (27-30 gauge).
The FIRST AID AND MEDICAL TREATMENTS AND SUPPLIES recommended in this brochure are based on information reported in the medical literature and the personal experience of Honeywell physicians. It should be noted that there are no medications in the U.S. for which the specific indication is the treatment of HF burns. The physician has the dilemma of using prescription drugs in a non-approved manner, or of using substances which are not approved drugs but which have been proven effective for medical treatment. Given the choice between recommending effective treatment, or recommending the use of only drugs which are approved, we have chosen to recommend the effective treatment.

Benzalkonium chloride (Zephiran) is available in the U.S. as a non-prescription drug. It is a surface active agent sold for use as a disinfectant. It is available in a 1:750 (0.13%) aqueous solution, a 17% concentrate, and a tinted tincture. The concentrated 17% solution must be diluted. The tinted tincture is not recommended to treat HF exposures.

CALCIUM GLUCONATE INJECTION, USP (one gram in 10 ml, 10% solution) is labeled for intravenous use only. Experience has shown that when diluted to 2.5% - 5% with normal saline, and used as described in this brochure, it is a safe and effective treatment for HF skin exposure. When diluted to 2.5% and used as described, it is safe for nebulization and inhalation, and when diluted to 1.0% and used as described, it is safe for eye irrigation.

NOTES

Caltrate® is a Registered Trademark of Wyeth Consumer Healthcare, Madison, NJ 07940

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This booklet describes the special First Aid and Medical Treatment measures necessary following exposure to or injury from HYDROFLUORIC ACID (HF).

However, it must be emphasized that PREVENTION of exposure or injury must be the primary goal.

Preventive measures include:

1. Making everyone who handles or uses HF aware of its properties and dangers.
2. Training everyone who uses HF in proper handling and safety precautions.
3. Utilizing all appropriate engineering controls, and making sure that the controls are maintained and functioning properly.
4. Requiring everyone who handles or uses HF to have available the proper safety and personal protective equipment, to be trained to use the equipment, and to always use the equipment when necessary.
5. Arranging ahead of time to provide first aid or medical treatment measures if necessary.

If you have questions, comments or suggestions, please write to:

Technical Service Manager - Hydrofluoric Acid
Honeywell Performance Materials and Technologies
101 Columbia Road
Morristown, New Jersey 07962-1053

Honeywell Hydrofluoric Acid

Recommended Medical Treatment for Hydrofluoric Acid Exposure