University of Iowa Materials Analysis, Testing, and Fabrication (MATFab Facility) Laboratory Manual

February 2023

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Introduction

Welcome to the University of Iowa Materials Analysis, Testing, and Fabrication (MATFab) Facility. We are managed under the Office of the Vice President for Research at the University of Iowa.

Mission: Our mission is to empower innovation and discovery in science and engineering by providing advanced fabrication and characterization of natural and engineered materials.

Vision: To be the premier facility for materials fabrication and characterization in the Midwest by offering state-of-the-art capabilities, technical expertise, and educational opportunities.

Values: Provide high quality data, technical support, and training for our users in a timely and professional fashion.

Our facility includes 5000 ft^2 of laboratory space in five laboratories within the Iowa Advanced Technology Laboratories (IATL). The MATFab facility houses instrumentation for chemical and elemental analysis, imaging, metrology, and micro and nanofabrication in one convenient location on campus. We are staffed by professional scientists with backgrounds in chemistry, engineering, geoscience, and physical sciences that allow us to meet research needs across many disciplines.

The goal of this manual is to provide important information about the facility in one document. It includes important contact information, information about the laboratory space, common laboratory practices, and safety information. Laboratory safety is a high priority for the MATFab facility. We work diligently with University of Iowa Environmental Health and Safety (EH&S) to ensure that our users are safe when in our laboratories. The guideline provided below are aligned with UI EH&S and other university policies, but provide some additional specifics related to our laboratories.

Important Contact Information

MATFab Director

Professor Tori Forbes, Department of Chemistry
Office: W374 Chemistry Building
Phone: 319-471-3430; email: tori-forbes@uiowa.edu

Contact the director if you have questions about billing, instrument acquisition, grant writing, or general information about the facility.

MATFab Staff Members

Schaffer Finney
Office: IATL 200
Phone: 563-349-3913; email: schaffer-finney@uiowa.edu
Responsibilities: Training and maintenance of fabrication equipment and cleanroom maintenance. Maintenance and use of Chemistry machine shop. Site specific training for IATL 172, 174 and machine shop.

Kenny Horkley
Office: IATL 114
Phone: 319-335-1828; email: lawrence-horkley@uiowa.edu
Responsibilities: Training and Maintenance of Electron Microprobe, X-ray Fluorescence, Scanning Electron Microscope (SEM), Bookit Lab Administrator.

Dr. Linhan (Leo) Li
Office: IATL 330
Phone: 319-335-0903; email: linhan-li@uiowa.edu
Responsibilities: Training and Maintenance of Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Laser Ablation Inductively Coupled Mass Spectrometry (LA-ICP-MS), and High-Resolution Inductively Coupled Mass Spectrometry (HR-ICP-MS). Site specific training for IATL 198.

Dr. Michael Sinnwell
Office: E323 Chemistry Building
Phone:319-384-1873; email: michael-sinnwell@uiowa.edu
Responsibilities: Training and Maintenance of BET pore analysis, elemental analysis, and chemical safety. Site specific training for IATL 170.

Dr. Daniel Unruh
Office: IATL 202
Phone: 319-384-1908 ; email: daniel-unruh@uiowa.edu
Responsibilities: Training and Maintenance of powder and single-crystal X-ray diffraction equipment and Raman spectroscopy. Site specific training for IATL 196.

IATL Building Manager
Krissy Dallmann
Building Coordinator
Iowa Advanced Technology Center - 105 IATL

205 N Madison St
Iowa City, IA 52242
Email: kristina-dallmann@uiowa.edu
Phone: 319-335-3313

University of Iowa Department of Public Safety
808 University Capitol Centre
200 S. Capitol St.
Iowa City, IA 52242
Email: police@uiowa.edu
Phone Non-emergency: 319-335-5022
Emergency: 911

University of Iowa Environmental Health & Safety
122 Grand Ave. Court
Iowa City, IA
Email: ehs-contact@uiowa.edu
Phone: 319-335-8501

Overview of the Laboratories

The MATFab facility occupies five laboratories within the Iowa Advanced Technology Laboratories (IATL) on the University of Iowa campus. All of the labs are on the first floor of the building. The equipment available in each laboratory is provided below.

IATL 170

Combustion Elemental Analyzer (CHN)
Microbalance
Carbon coater
Gold Coater
Oxidation Furnace
Thermal Evaporator
VWR vacuum oven
RTP annealer
Chemical Fume Hood

IATL 172

Optical Profiler
Ellipsometer
Raith Voyager Nanolithography

IATL 174

Sputterer
Mask Aligner
Atomic Layer Deposition
Electron Beam Deposition
RIE ICP Plasm Pro
RIE NGP80
Nanonex 1000
Solvent Bench
Negative Resist Spin Coater

IATL 196

D8 Advance Power X-ray Diffractometer
SmartLab Powder X-ray Diffractometer
Single-crystal X-ray Diffractometer
BET Instrument
X-ray Fluorescence Spectrometer

IATL 198

Electron Probe Microanalyzer
Inductively Coupled Plasma-Optical Emission Spectrometer
Inductively Coupled Plasma Mass Spectrometer
Scanning Electron Microscope

Hours of Operation

After appropriate training, users will gain access to the laboratories and the building. The laboratories are available to users 24 hours a day 7 days a week. Staff will be available to support users during normal working hours (Monday – Friday, 8:00 a.m. – 5:00 p.m.). **NOTE: Never work alone at a potentially dangerous activity.** If you utilize the laboratory outside normal working hours, please make sure that you notify a lab partner or family member so that they are aware of your presence in the laboratory.

Basic Laboratory Rules

1. Occupants of the MATFab laboratories should be 18 years or older. Exceptions to this rule include authorized tours that are led by a designated staff or faculty. Minors who would like to utilize the equipment would have to abide by the established guidelines for Minors on Campus Policy. This includes registration with the university and supervision within the laboratories at all times by the PI. The PI is required to undergo criminal background checks and Minor on Campus training if they plan to have minors working in the laboratories. In addition, the PI is required to get permission from the MATFab director and provide a written research plan and identification and mitigation of all hazards. Minors are not permitted to work with radioactivity, toxins or carcinogens, corrosive or volatile chemicals, explosive chemicals or agents or organic solvents.
2. Users should not allow unauthorized persons into the laboratory. If someone has not gone through proper safety training, then they cannot be there without authorization of the staff or director.
3. All users must wear long pants and closed-toe shoes for entrance into any MATFab facility.
4. As in any area in which chemicals are used, eating and drinking are prohibited in all of our laboratories. If you have a water bottle or beverage, please leave it on the floor or the tables located by the laboratory entrance.
5. Users may use cell phones in the laboratories, but headphones are not allowed in IATL 170, 172, 174 due chemical hazards. Connecting your phone, tablet, or laptop into any instrumentation in the laboratory is prohibited.
6. Do not tamper with computer monitors, Bookit relays, or instruments without direct permission of the MATFab staff. Unauthorized use of MATFab computers, electronic devices, or equipment could result in disciplinary action.
7. Removing data from the instruments should be performed using the University of Iowa network or by email where possible. Flash drives and external storage drives are not allowed for data transfer.
8. Laboratory users must act in a professional manner at all times. Professional behavior in the laboratory includes punctual instrument use (as based upon Bookit Lab schedule); prompt notification of tardiness, absence, or time-delays related to instrument use and training; demonstrating respect to staff/faculty/users; maintaining professional integrity and honesty in all research activities/interactions; representing accurately the instrument hours utilized; using appropriate professional language (spoken and written) in communication with staff and users; demonstrating a willingness to resolve difficult relationships and modify behavior accordingly; not expecting special consideration outside of MATFab policies; demonstrating non-defensive receptivity to feedback and suggestion.
9. Be aware of your surroundings and move carefully as you work in the laboratories. The laboratories house expensive complex instrumentation, compressed gas cylinders, and

valuable samples. Please make sure you are not running or moving too quickly within the laboratory to prevent injuries and damage.

10. Make sure that you notify staff when the instruments are not operating correctly. If troubleshooting guides are available, users are allowed to go through simple troubleshooting procedures. However, staff must be present if additional troubleshooting or maintenance is required. **When in doubt, contact a staff member!** Damage to the instruments and users is possible without proper training.
11. Users should only utilize instrumentation based upon the protocols provided by the staff. If there are needs outside of the stated protocols, user must contact the MATFab staff for approval.
12. Make sure that doors are properly closed when you leave the laboratory.

Gaining Access to the facility and training

1. The first step is requesting access to the Bookitlab software so that you can reserve instruments for training and use. The website is here: https://core.bookitlab.com/uiowa/Login.aspx. To create a new user profile, click the button underneath the sign-in labeled "new user" and fill out the requested information. You will need to be affiliated with a user group. If the PI or research group is already in the system, then you can choose their name from the list. If the PI research group is not listed, then you should find the "New User" group. If you are in the new user category, then you must contact the staff (matfab-staff@uiowa.edu) to indicate what research group needs to be added to the system. The staff will contact the PI to request additional information about the billing account (MFK) for usage and then the new user will be moved into the proper PI research user group.
2. Online safety training courses must be completed before training can be completed and access to the lab(s) granted. The required ICON training list is below:

   W115OS (HazCom with GHS)

   W008CM (Lab Chemical Safety)

   W157CM (PPE Awareness for labs)

   W07HAZ (Hazardous waste for labs)

   W485CM (Chemical Fume Hoods)

   W524HZ (Biohazardous waste bin training)

   The information regarding the above ICON courses can be found here: https://ehs.research.uiowa.edu/icon-safety-training-information. Please provide documentation that the above ICON training courses are complete by emailing documentation to the MATFab staff (matfab-staff@uiowa.edu). NOTE: Some of the above train courses are required annually. It is the responsibility of the PI to confirm that all of the necessary training is completed annually and that students are aware of the PI's Chemical Hygiene Plan and PPE HAT associated with the PI's own laboratory.

3. After ICON online training is complete, please contact the MATFab staff (matfab-staff@uiowa.edu) to arrange onsite safety training and for instrument specific training. Please see page 4 for staff responsible for instrument and site specific training. Users are not allowed to use the instruments independently until they have approval from staff.

Cleanroom gowning procedure

The cleanrooms in IATL 172 and IATL 174 have a gowning requirement for entry. The gowning procedure is outlined below:

1. Grab a pair of shoe covers from the bin located at the entrance to the clean space. Do NOT put them on. NOTE: If the shoe cover that you grabbed has a hole in it, dispose of it in the waste bin.

Figure 1. Step one of the gowning process – Shoe covers are in the red bin.

2. With the shoe coverings in your hand, enter the gowning area placing both feet on the tack mat. Taking a few steps in place will help with keeping our clean space clean.

Figure 2. Step two of the gowning process – Make sure you step on the tack mat.

3. Place the shoe coverings over your shoes.
4. Put on a hairnet. NOTE: Do this FIRST, before putting on gloves, to avoid contamination of your gloves.
5. Put on a facemask.
    a. If the facemask has elastic ear loops then it will go on now, before the head covering.
    b. If the facemask ties behind the head then it will go on after the head covering.
6. Put on gloves.

Figure 3. Users should don their (1) shoe covers (2) hairnet, (3) facemask, and then (4) gloves.

7. Choose a new head cover then remove it from the bag and put it on with the tag facing inwards.
   - Snap the two front snaps.
   - If the facemasks tie behind the head then now is the time to put it on.

Figure 4. Step seven of the gowning process - User with headcover on.

8. Remove a new gown from the bag and put it on with the neck portion of the head covering fitted underneath, inside of the gown. NOTE: It is usually a good idea size up because of the placement of leg snaps.

Figure 5. Step 8 of the gowning process. The neck of the head cover goes under the gown.

9. Put on a pair of shoe covers based on your size of shoe.
    - Buckle the shoe cover.
    - Snap the top of the shoe cover to remove some slack.
    - Snap the shoe cover to the gown so that they do not fall down.

Figure 6. Step nine in the gowning process showing the process of snapping the boot strap (left) and the leg strap (right). Also note that the shoe cover is buckled to keep in place.

Figure 7. User with completed gowning.

10. When finished in the lab, and if returning, put a tag on a hanger with your name. If not returning you should still hang your gown but do not use a tag.

Figure 8. Step 10 of the gowning process shows tagging the gown for return use.

11. Return the shoe coverings to the bin at the entrance as you leave.

NOTE: Gowns will be changed approximately every 2 weeks. If your gown becomes contaminated then place it on the floor of the gowning area and notify a staff member.

Sample Preparation for Characterization

1. We prefer that users utilize their own wet bench facilities to prepare their samples into the required form for analysis if possible.
2. If a user does not have access to their own wet benches then they can contact a staff member to discuss.
3. MATFab has access to wet bench space and equipment (ovens, furnaces) to prepare samples that can be reserved on BookItLab.
4. Staff members may assist in the preparation of samples for analysis but staff time will be charged and the staff member will have the right to refuse assistance.
5. Samples that can be considered a biohazard must be approved before working with these types of materials in the facility.

General Chemical Safety

1. Use of any wet benches or the normal handling or transportation of any chemicals in the lab requires the use of PPE. Disposable gloves, safety glasses, and lab coats are stocked

in all labs at the MATFab laboratories. Eye protection in the form of safety glasses or goggles should be always worn in the lab unless you are sitting at an instrument computer. The exception is when using a microscope or equipment with eye pieces. For users requiring corrective lenses, impact-resistant prescription safety glasses with side shields may be purchased from most prescription glasses suppliers. Contact lenses are allowed, but safety glasses are still required for laboratory activities. Most safety glasses are designed to protect only against flying fragments, however, not chemical splash hazards. So full face shields or use of the hood sashes should be worn in addition to glasses when working with hazardous chemicals at the wet benches. Contact a staff member (matfab-staff@uiowa.edu) if you require additional PPE for work in the MATFab Facilities.

2. Users must first be trained in wet bench usage and always reserve the bench before using. If a user is caught using the benches without a Bookit Lab reservation the PI will be notified, and multiple infractions can result in access to the lab being revoked.
3. Use of corrosives that are greater than 2 M (molar) for etching or sample preparation can only be performed between the hours of 8 a.m. – 5 p.m.
4. Chemicals can only be brought into the laboratories as working solutions or as chemicals associated with a PI's inventory. A PI must have their own chemical inventory through UI EH&S and also submit their MATFab chemical inventory (see Appendix 1 for information on the proper form) for approval to the MATFab staff member in charge of chemical safety (see page 4). Users will need to provide information about volumes, compatibility with other chemicals, and storage requirements.
5. Chemicals can only be stored in designated chemical storage spaces in 170 and 174 that are specific to the PIs labs and are approved by the staff member in charge of chemical safety. To add chemicals to the MATFab storage, you must contact the MATFab staff member in charge of chemical safety for approval. All chemicals will need to be labeled properly (Stickers are available with user name, PI name, chemical formula, date) and will be disposed at the expiration date (contact MATFab staff if you have concerns about disposal). Proprietary names do not count as chemical formulas and additional information must be provided on the label. If this information is not available, then chemical class (organic/flammable/corrosive) must be included on the label. **DO NOT LABEL GLASS BOTTLES WITH SHARPIE.** Organic solvents will dissolve the label and result in an unknown, unlabeled solution. Use a proper paper label or put tape over the sharpie label so that it does not dissolve. Any chemicals not properly labeled, stored outside of the designated cubby or not included on the chemical inventory will be removed by staff members and a disposal fee ($165) will be charged to the user's account.
6. Working solutions (solutions that are not in their original bottle) can only be stored in the space designated as chemical storage space and must be labeled with user name, PI name, chemical formula, date.
7. Chemical Waste policy – Individuals must provide their own labeled waste bottles for their own individual processes. Each chemical added to the bottle must be clearly written on the label. **DO NOT DATE THE LABEL.** These need to be stored in the appropriate waste collection area. These waste storage areas are labeled as acid, base, and organic solvent. **WASTE STREAMS SHOULD NEVER BE MIXED.** Waste bottles are available in Chem Stores (Chemistry Building) and need to be provided by the user. The exception to this is HF wastes (detailed in Appendix 2). A chemical inventory and waste monitoring fee ($70) will be charged monthly to the users account if they house chemicals in the MATFab facility. If improper waste storage or disposal is observed a fine of $165 will be

charged to the users account and PI will be notified. Multiple infractions can result in access to the facility being revoked.

8. Laboratory bench space is available for use in 170 for creating solutions and preparing samples. Glassware is available in the laboratory but must be cleaned, dried, and put away after a user has finished their work.
9. Do not leave an experiment on a hot plate overnight, even if the hotplate is turned off; NEVER leave a hot plate turned on overnight. If you must leave a hot plate unattended, please label your experiment with your contact information and chemicals/materials that are on the hot plate. Label with lab tape affixed to bench in front of hot plate. Cover beakers with glass plates. Avoid the use of loose paper towels or Kim wipes in the fume hoods and laminar flow hoods as these can be blown into the exhaust and cause flow issues.
10. Working solutions should be labeled and are not allowed to be left unattended in the laboratories. If unlabeled solutions are left on any wet bench they will be removed, identified and a disposal fee will be charged ($165).
11. Chemical spills should be reported to the MATFab staff who will direct appropriate clean up procedures. Failure to report spills will result in removal of laboratory access. General-purpose spill kits for most acid, solvent, and mercury spills are in 170 IATL and at the end of the hall near the 170 IATL entrance for spills in 174 and 172 IATL. All work with acid is limited to 170 IATL. A hydrofluoric acid spill kit is located near the acid bench fume hood in 170 IATL. A complete spill response guide is located in the laboratory spill kits.

Information about proper use of fume hoods within the MATFab Facility

1. All proper training must be complete and PPE must be worn at all times. If you are found by MATFab staff not wearing proper PPE, a notice will be sent to the laboratory PI and you will be required to retrain on the acid bench. Two notices means that you will no longer be able to utilize the MATFab acid bench.
2. For the chemical fume hood in 170, users should have the sash between themselves and chemicals that represent a splatter or reactivity risk. When not in use, the sashes should be kept closed to prevent flow issues.
3. The acid bench (chemical fume hood in 170 IATL) should be used for all acid work. **NO ORGANIC SOLVENTS OR BASES ARE ALLOWED IN ACID BENCH**. Only one acid at a time is allowed to be used in this hood. This includes Nanostrips/piranha solutions, hydrofluoric acid, and metal etchants. This means that each user needs to fully remove all working solution, samples, glassware, and waste after each use so that it is clean for future users. Waste should be stored in the appropriate waste disposal area for corrosives. Anything left in the hood prior to use should be reported to the MATFab staff.
4. Hydrofluoric acid waste and calcium hydroxide HF neutralizing solutions and creams are stored at the acid bench in the fume hood; see Appendix 2 for additional information on HF safety and handling. Special precautions must occur for the acid bench in 170 where HF is utilized, and HF waste streams must be kept separate from all other acids.
5. Piranha solutions (sold as Nanostrip) are also extremely hazardous chemicals to work with and will react violently with many other chemicals. See Appendix 3 for additional details working with this solution.
6. Concentrated Nitric acid is also extremely corrosive. If you spill nitric acid **DO NOT CLEAN WITH PAPER TOWELS**. This can cause fuming and spontaneous combustion to potentially occur.

7. The solvent bench in 174 is a laminar flow bench. Note that this is not a chemical fume hood and users should make sure the floor of the hood is clear to allow for proper airflow. Two hot plates and spin coaters are kept permanently in the solvent bench in 174; users must be trained on this equipment before use.

Information about compressed gases within the MATFab Facility

1. MATFab staff oversee handling, changing regulators, and ordering compressed gasses in the facility. Users should not handle the compressed gas cylinders without permission from the MATFab staff.
2. Boron trichloride and chlorine gas are the only toxic gases in the MATFab that pose a significant health hazard. Both gases are highly corrosive and are stored in an exhausted gas cabinet in 174 IATL which is equipped with an alarm in case of loss of air flow from the exhaust manifold. If you notice an alarm in 174, please notify MATFab staff immediately.
3. House nitrogen and compressed dry air (CDA) are plumbed throughout the facility for general use in equipment and other utilities. The supply can run up to 80 psi, which can pose a hazard: do not direct a nitrogen or air gun toward your own body (especially the face and eyes) or toward anyone else.
4. Tetrafluoromethane (CF_4), Oxygen (O_2), and Trifluoromethane (CHF_3) are commonly used in dry etching. Although the gases themselves generally pose low health risk, their by-products in etch systems are less benign. Make sure to follow proper operating procedures for pumping down or purging etch chamber systems following processing. Failure to do so could result in removal of access to the instrument.
5. Nitrogen is stored in liquid form inside the 174 and 196 laboratories and is evaporated to be delivered to certain instruments and equipment in the gas phase. Liquid nitrogen should not be used in an enclosed space because of the risk of asphyxiation. Liquid nitrogen can also burn tissue on contact, so protective gear must be worn whenever handling.
6. Argon is stored in liquid form in laboratory 198 and is evaporated to be delivered to certain instruments in the gas phase. Liquid argon should not be used in an enclosed space because of the risk of asphyxiation. Liquid argon can also burn tissue on contact, so protective gear must be worn whenever handling.
7. Liquid helium is also present in a closed loop on the Angstrom e-beam evaporator in 174 IATL and poses little no health risk to users. Evidence or sign of leakage of this loop should be reported immediately to a MATFab staff member.

Information about usage policies and disciplinary action

The information provided in this laboratory manual is intended to provide expectations and guidelines necessary to keep the lab running smoothly. Many of these guidelines are simply common sense and require consideration of the other laboratory users. Others require specific knowledge of either proper equipment use or of chemical handling and safety. Please communicate with the MATFab staff or director if you have any question or concerns while using the facility.

1. It is the user's responsibility and obligation to be trained on a particular piece of equipment or to be aware of correct chemical handling procedures. If a user does not have these skills, please request training from a MATFab staff member before performing the task. Information on training is available on the MATFab website. MATFab staff are responsible for ensuring that the initial safety training requirements are met, but the PI is responsible for ensuring annual renewals are met.

2. MATFab staff and users can at any time request a stop work order if they see anything dangerous occurring in the laboratory. Users should contact a MATFab staff member if they have any safety concerns. The staff will consult with the director to determine the correct course of action.
3. The guidelines are subject to revision dependent upon laboratory procedural changes. Changes will be communicated to the users either by email or through user meetings.
4. Please encourage proper facility usage among other users and report any serious violations of the guidelines to lab staff.
5. The following procedure will be used to discipline offenders in the laboratory. For each offense by a particular individual, the following three step system will be used:

   • First Offense: The individual will meet with the MATFab staff in charge of the specific instrument or laboratory. If the offense was a rule the individual was unaware of, the correct information will be provided, and an official warning will be given that will be documented via email to the user and the MATFab director. If the offense was more severe, the information will also be sent via email to the advisor. This determination of the severity will be made by the MATFab staff member.

   • Second Offense: The individual will meet with MATFab staff member, MATFab director, and advisor. The corrective action will then be decided by this group. This action may include suspension of lab use, retraining, and/or charges billed to the user's account for clean-up/handling of the infraction by MATFab staff. This second offense will also be documented via an official memo on university letterhead and emailed to all parties.

   • Third Offense: The individual will be suspended indefinitely from the laboratory and/or charges will be billed to the user's account for clean-up/handling of the infraction by MATFab staff. The issues will be officially documented on university letterhead and distributed to all parties.

APENDIX 1 – Additional Information on PI Chemical Inventory

As stated on page 9 of the MATFab Laboratory Manual, PIs must maintain their own chemical inventory using the EH&S system. In order to store chemicals in the MATFab Facility, we need additional information on the chemicals stored within the facility. To bring chemicals into the facility, it needs approval by the MATFab staff member in charge of chemical safety and maintain a list of their inventory holdings.

The MATFab chemical inventory (excel spreadsheet) for each PI must be filled out prior to bringing chemicals into the laboratory. Information required includes:

PI name

Approved users

Date of latest update of inventory

Chemical name

Chemical formula

Volume

Incompatibles

Storage Location

Process Details

Waste Plan

This document must be emailed to the MATFab staff person in charge of chemical safety. They will provide written approval for addition of the chemical to the list and provide information on proper storage expectation. If the user has questions, they may contact the MATFab staff to determine the best location.

APENDIX 2 – Detailed guidelines for using hydrofluoric acid (HF) in the MATFab Facility

*Portions of this section have been repeated from the EHS section on Hydrofluoric Acid Safety Guidance which can be found at https://ehs.research.uiowa.edu/hydrofluoric-acid. Much of the information for this guide is taken from the peer reviewed publications: *ACS Chem. Health Saf.* **2020**, 27(3), 183–189 (https://doi.org/10.1021/acs.chas.0c00008),*Chem. Health Saf.* **1998**, 5(5), 25– 28; *Chem. Health Saf.* **2000**, 7 (1), 18– 23 (https://doi.org/10.1016/S1074-9098(99)00077-5).

Before working with HF, it is important to understand the (1) Hazards, (2) Treatment, (3) Controls: Training/Administrative, (4) PPE, (5) Controls: Engineering, (6) Storage, (7) Waste Handling, and (8) Spill Management and Reporting. All users must undergo hands-on HF training with a MATFab staff member prior to any work with HF.

Hazards

HF is considered a highly hazardous chemical because of its strong corrosive nature, but more importantly for its acute toxicity, warning signs and symptoms, and delayed health effects (NFPA health hazard rating 4). HF poses a risk from all routes of entry: ingestion, inhalation, injection, and absorption. It is ranked as one of the most hazardous materials to human health as concentrated HF covering 2% of the body can be fatal.

A common route of occupational exposure in research labs is skin contact with HF solution or droplets. The fluoride ions are very rapidly absorbed through the skin and eyes and cause systemic toxicity. HF progressively releases fluoride ions and the 'free fluoride ions' penetrate and spread into the deepest tissues and form insoluble salts with calcium and magnesium, resulting in liquefactive necrosis (also known as colliquative necrosis, tissue death that liquefies the affected cells), hypocalcaemia (low calcium levels), hypomagnesaemia (low magnesium levels), and hyperkalemia (high potassium levels). The liquefactive necrosis mechanism differentiates HF from other acids, e.g. sulfuric (H_2SO_4), hydrochloric (HCl), nitric (HNO_3), or acetic (CH_3COOH), which cause damage via the 'free hydrogen ions', thus causing coagulation necrosis with precipitation of the tissue proteins.

HF is very reactive. HF attacks glass, ceramics, concrete, metals, some forms of plastic, rubber, and coatings. HF is reactive with most bases, acids, and oxidants and produces toxic and corrosive fumes upon reaction with water or steam. Below are some examples of reactions with common chemicals found in acid-neutralizing spill kits and highlight the unique and dangerous nature of HF:

- The exothermic reaction of Na_2CO_3 or K_2CO_3 with HF generates sodium or potassium hydrogen bifluoride ($NaHF_2$ or KHF_2) intermediates, which can release gaseous HF.
- The exothermic reaction of KOH or NaOH with HF also generates potassium or sodium hydrogen bifluoride ($NaHF_2$ or KHF_2) intermediates, which can release gaseous HF.
- Silicon-based absorbent materials react with HF to generate silicon tetrafluoride, which is a toxic and corrosive gas.

People have died because of HF exposure.

Treatment

Injury and illness prevention is the most significant part of HF management in research labs because internal damage can occur before symptoms appear. Pain associated with exposure to

solutions of HF may be delayed for 1-24 hours. Even dilute solutions can lead to serious health risks. **If HF is not rapidly neutralized and the fluoride ion bound, tissue destruction may continue for days and result in limb loss or death**.

First aid measures **MUST BE** started within seconds in the event of HF contact in any form or concentration!

Researchers must then seek immediate medical attention for HF burns by going to the UIHC EMERGENCY TREATMENT CENTER (ETC). If no one is immediately available to assist you or drive you to ETC, call 911 and let them know you have a medical emergency with HF exposure.

1. Skin exposure: Immediately (within seconds) shower or flush with plenty of water. Remove all clothing while in the shower (remove goggles last; double-bag contaminated clothes). Because calcium gluconate gel (2.5%) is available, rinsing can be limited to 5 min (this is sufficient time to effectively remove HF from the skin; additional flushing time may be unnecessary and will delay further treatment). Apply calcium gluconate gel (2.5%) while wearing impervious gloves en route to medical attention. Massage the gel promptly and continuously into the burned area. Injections by medical personnel of 5% calcium gluconate (CG) may be required within 20-30 minutes of exposure.
2. Eye Contact: An individual will need to seek medical attention at the ETC as soon as possible. If the spill has occurred near the eye, eyelid, or eyelash, irrigate exposed or irritated eyes with cold water for:
    a. 5 mins if a calcium gluconate (CG) eye wash solution is readily available and is used immediately after the 5 minutes of cold water rinse.
    b. at least 20 minutes if a calcium gluconate (CG) eye wash solution is not readily available.
3. Ingestion: Drink large amounts of water. Do not induce vomiting or administer activated charcoal. Drink several glasses of milk or several ounces of milk of magnesia, Mylanta, Maalox, or similar product, or up to 30 Tums, Caltrate, or other antacid tablet. Get immediate medical attention.
4. Breathing Vapor: Breathe fresh air right away. Breathe 100% oxygen as soon as possible. If necessary, trained personnel could provide 2.5% calcium gluconate solution by nebulizer.

Controls: Training/Administrative

Users must reserve the acid bench fume hood using the online scheduler before anticipated work with HF

Users cannot work alone with concentrated HF in the lab. Work with dilute HF must be performed during working hours. A second individual must be informed of your anticipated work with HF and the PI must be onsite when work is being performed with concentrated HF.

Standard operating procedures (SOPs): Before a user can begin any work with HF, they must submit an SOP for their work and experiments to be performed at the MATFab. This SOP should include the following sections and must be submitted to a MATFab staff member.

- Purpose of experiment
- Reagents and labware items: List all reagents and equipment needed for the experiment including concentrations and anticipated volumes of chemicals per experiment
- Experimental method

- Describe the experimental steps to be performed in the acid bench fume hood at the MATFab

Any updates or revisions to a user's SOP that pertain to new chemicals or chemical mixtures and corresponding waste must be submitted to a MATFab staff member.

PPE

When working with HF, safety glasses with side shields are NOT adequate. Outer neoprene, nitrile, or butyl rubber gloves (14 mil or thicker), inner double nitrile gloves (4 mil thick), butyl rubber apron, face shield, chemical splash goggles, lab coat, long pants, and closed-toed shoes must all be worn at all times. Hydrofluoric acid-specific PPE for work at the 170 IATL acid bench can be found in the cabinet located adjacent to the acid bench work area as shown in the Figure below. This cabinet is for HF PPE only and should not be used to store any other materials to avoid HF transfer to other PPE/surfaces.

Controls: Engineering

All tools and labware that come in contact with HF during an experiment should be made of polyethylene, polypropylene, or polytetrafluoroethylene plastic

All work involving HF or other HF-containing reagents must be performed inside the acid bench fume hood in 170 IATL

Small lab tools that have come in contact with HF should be rinsed in the acid bench's calcium hydroxide bath (known commercially as Kolor-Safe® / Kolor-Lock ®) prior to final rinsing with DI water (see Figure below). A fresh, 1 L bottle of 12 wt% Kolor-Safe ® is located in the acid bench fume hood and should not be used to replenish the Kolor-Safe® bath.

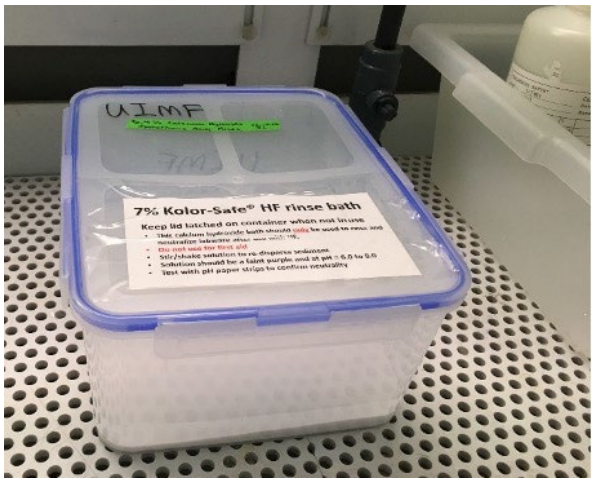

Figure A2-1. Calcium hydroxide bath location for HF neutralization.

Users are not permitted to leave the acid bench area wearing PPE used to work with HF nor leave open containers/labware with HF unlabeled or unattended

A plastic bottle carrier should be used for transporting HF bottles between the storage cabinets, the acid bench, and hazardous waste pick-up locations.

When finished working with HF, inspect all gloves and apron for HF droplets and place these items back in their appropriate storage location. Place all disposable PPE in the red biohazardous waste bin located in the acid bench work area

Wipe any suspected HF droplets with a Kolor-Safe®-soaked-towel followed by clean-up with DI water to remove any calcium fluoride residue.

A fresh, 1 L bottle of 12 wt% Kolor-Safe® is located on the back shelf of the acid bench fume hood and can be used for clean-up with towels. Dispose of all towels in the red biohazardous waste bin.

Researchers must thoroughly wash their hands after handling HF bottles and reaction vessels

Storage

Users are not permitted to store their own HF at the MATFab and are strongly discouraged from transporting open HF bottles between labs in IATL. If your HF requirements are not being adequately met, please inform a MATFab staff member

Users must be informed of all storage locations for both stock and waste HF solutions

Never store or use HF with glass materials/containers or place HF containers in a location that has not been designated for HF storage by a MATFab staff member.

Waste Handling

Waste disposal: Include method for neutralizing and cleaning all tools that have come in contact with HF. This typically includes rinsing tools in a calcium hydroxide bath prior to final rinsing and drying. List out anticipated waste mixtures including all components and their approximate concentration in the waste mixture in weight percent, including anticipated volume of waste per experiment. If HF waste contains hydrogen peroxide (H_2O_2) it must specifically be put into the HF/H_2O_2 waste

Waste disposal - In addition to these practices for handling HF waste, all users should follow standard hazardous waste storage practices and labeling procedures.

1. HF on labels should be written out as hydrofluoric acid, not “HF.”
2. Never pour HF waste down the drain. If small amounts of HF are accidently spilled in the acid bench sink, sprinkle with Kolor-Safe® and flush with copious amount of water. See Spills section.
3. Do not mix HF with other laboratory generated waste
4. All containers used to store HF waste should be made of polyethylene, polypropylene, or polytetrafluoroethylene plastic
5. Never store or use HF waste with glass materials/containers—HF is highly reactive with silica and will attack glass bottles and form toxic SiF_4
6. HF waste storage at the MATFab is limited to no more than five, 1 L Nalgene bottles located in the storage bin under the acid bench fume hood as shown in the figure below. When you add waste to the bottle, make sure that any chemical components are included on the waste bottle. Once a bottle is full, the user must notify MATFab staff for pick up.
7. If HF waste also contains hydrogen peroxide (H_2O_2), keep the HF/H_2O_2 waste in the HF waste storage bin shown. All H_2O_2 waste mixed with a bench acid must be placed in a glass bottle. To prevent waste bottles from exploding or bulging, users should make sure their waste bottle is in a secondary containment bin and leave the lid slightly loose to relieve oxygen gas build-up. All H_2O_2waste bottles should be stored in the corresponding

red bin located near the front of the lab. If the H_2O_2 waste is also mixed with chemicals that give off toxic vapors (e.g. hydrofluoric acid, hydrochloric acid, etc.), these bottles should be stored in a secondary containment bin in a fume hood. Again, please consult a MATFab staff member for appropriate handling of your H_2O_2 waste.

Figure A2-2. HF waste storage bin for 1 L Nalgene waste bottles.

Spill Management and Reporting.

An HF spill kit is located to the left of the acid bench fume hood on the floor in an orange bucket as shown in the figure below. The content of this HF first aid and spill kit should be verified by all users prior to their first work with HF. MATFab staff will verify the contents of this kit at the start of each work week. **If you spill HF you should notify MATFab staff immediately. Do not attempt to clean up an HF spill by yourself.**

APPENDIX 3 – Proper usage of Piranha solution in the MATFab facility

The piranha solution described here is for the acid form (also called Caro's acid), which contains 30% hydrogen peroxide and concentrated sulfuric acid. There is also a basic version that is formed from combining hydrogen peroxide and ammonium hydroxide. We are not discussing the base form in this appendix. The acid piranha solution also has commercial names such as "Nanostrip" or "NoChromix". While the commercial versions are considered stabilized solutions, the risks associated with working with them are similar to that of working with plain piranha solution so the MATFab facility considers them the same. Much of the information for this guide is taken from the peer reviewed publication by Schmidt (2022) *ACS Chem. Health. Saf.* 29, 54-61 (https://doi.org/10.1021/acs.chas.1c00094).

Before working with Piranha, it is important to understand the (1) Hazards, (2) Treatment, (3) Controls: Training/Administrative, (4) PPE, (5) Controls: Engineering, (6) Storage, (7) Waste Handling, and (8) Spill Management and Reporting. All users must undergo hands-on Piranha training with a MATFab staff member prior to any work with Piranha.

Hazards

There are numerous risks to using piranha solution that the user must be aware of before using. **This acid is highly corrosive to human skin, eyes, and mucus membranes.** It is highly reactive with any organic substances and will corrode most metals. Permissible exposure limits are 1 ppm. **Piranha solution may also spontaneously ignite when in contact with organic substances**. There is also the possibility of explosions due to the breakdown of the hydrogen peroxide (rapid release of oxygen) and release of hydrogen peroxide vapor. Piranha solution will form a highly explosive compound when it reacts with acetone to produce triacetone triperoxide (TATP).

Treatment

Always be aware of the danger signs when working with Piranha solution. If the solution foams or smokes, this suggests an instability of the system and the user should close the sash on the fume hood and report this to the MATFab staff. If a solid organic phase (usually a white solid) forms, then immediately leave the area and notify the MATFab staff. The white solid may be TATP and would require immediate evacuation.

If you spill Piranha solution on your clothing, skin or eyes, the area should be flushed for 15 minutes with water and seek medical attention.

Controls: Training/Administrative

You must have express permission from the MATFab staff if you are going to work with Piranha solutions in the facility. You must be fully trained and approved to perform the experiments before use. You must consult with the MATFab staff on the exact procedure you plan to do and how you will manage the waste solutions before working with Piranha solutions.

Users should not work alone when using piranha solutions.

Piranha solution may only be used during normal working hours, when MATFab staff are available.

During the cleaning process, the user should remain in the laboratory and never leave a sample unattended.

PPE

Users should don the following PPE: safety googles, laboratory coat, neoprene gloves. As with all work in the facility, users should have long pants and closed-toe shoes.

Controls: Engineering

Piranha can only be used in the chemical fume hood in 170. Since this hood serves as the acid hood, the user must make sure the hood is clean and free from other acids, wash bottles, or waste bottles before use.

While working with Piranha solution in the acid hood, the sash should be placed in front of the user so that there is additional splash protection.

Pyrex glass should be used for any solution in contact with piranha solution. Teflon tweezers should be used to deposit and retrieve samples.

All items should be washed, cleaned and dried (preferably with a nitrogen gun) before being placed into the Piranha solution.

After the cleaning process is complete, the sample should be placed in a DI water wash for five minutes before placing into a second DI water wash for an additional rinse for five minutes.

Storage

Users are not permitted to store their own Piranha at the MATFab and are strongly discouraged from transporting open Piranha bottles between labs in IATL. If your Piranha requirements are not being adequately met, please inform a MATFab staff member

Users must be informed of all storage locations for both stock and waste Piranha solutions

Never store or use Piranha with organic materials or place Piranha containers in a location that has not been designated for Piranha storage by a MATFab staff member.

Waste Handling

The Piranha solution should be neutralized before disposal by diluting to 10x the original volume with DI water. Then add sodium bicarbonate slowly while stirring with a glass rod until no more powder dissolves. The pH should be checked with a strip to make sure it is in a neutral pH range (approximately 7). The solution should sit in the original container until the user confirms that no bubbles are forming from a continued reaction with the sodium bicarbonate.

After neutralizing the solution, the waste should be placed in a clearly labeled waste bottle with a vented cap. Make sure that there are no chemical reactions occurring when you place the Piranha into the waste container. This could include the formation of bubbles, smoke, vapors, or solid crystals. All of these are an indication that there could be an explosive risk.

Spill Management and Reporting

In the event of a spill, notify a MATFab staff member immediately and they will assess the correct course of action regarding clean-up.