



# Nanoscale Fabrication & Characterization Facility (NFCF)

## Acid/Caustic Hood Safety and Operation Procedures Manual

(9/22/2021)



The Acid/Caustic Hood is equipped with sink, de-ionized water supplied at 18 Mega ohms per cm squared resistivity, acid waste disposal, caustic waste disposal, dry nitrogen and vacuum connections. There are digital timers, and stirring hot plates available as needed.

For emergency assistance call 412-624-2121.

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## Updated operation notes(Aug2021)

- 1) Waste bottles for HF/BOE and Piranha are inside the hood, all the rest of the waste bottles are under the hood. Upon using the waste bottles, handle the tray together with the bottle to move up and down. Please be super careful as the little hole on the waste bottle is left open!
- 2) Two 2<sup>nd</sup> containers inside the hoods are used for long time processing in HF/BOE, or Piranha solution. Please label with your name, phone number and date when use it. For short time processing, DO NOT use them. For Piranha, remember that the solution can be as hot as 130C, so it's recommended to make up the solution inside the 2<sup>nd</sup> container. If you already make up solution outside the 2<sup>nd</sup> container, do not attempt to move the beaker into the 2<sup>nd</sup> container (hot and extremely dangerous).
- 3) For longtime processing, it's only allow for overnight in Piranha, and no more than 48 hours in HF/BOE. For even longer processing time, please discuss with NCF staff.
- 4) All the acids/peroxides are stored in the new cabinet nearby, separated in different trays. Please handle the bottles with great care!
- 5) Both the hood and cabinet are locked. Keys are stored in the pass-through locker.

## Policies

- Only acid etching or base etching can occur at one time in the "Acid hood"
- Etching with acid and base solutions at the same time is NOT permitted
- Notify NCFD Director of any spills of acid or base solutions that occur
- Clean-up any spills of acid or base solution
- Wipe down the "Acid/Caustic hood" bench top after completion of the (acid or base) etching process
- Properly collect acid and base waste solutions in separate, properly labeled containers
- To mix any acid with other solutions, send detailed procedure to NCFD staff for review before use. Only approved process can be allowed

## Basic user guide

- 1) All users must read and understand the Safety Data Sheet (SDS) for ALL chemicals listed for use in the Acid hood. This information gives you details of the hazards and what can happen and how to respond if an accident occurs. All SDS documents for the chemicals allowed in the acid bench are located in the three ring binder located at the bench.



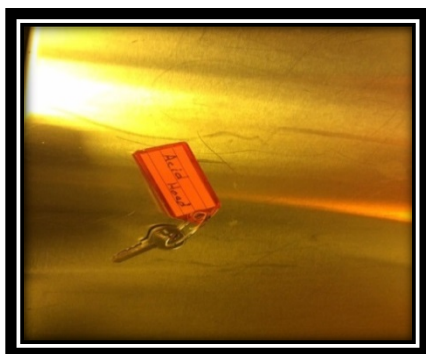
### Chemicals list for Acid

Lactic Acid	Nitric acid
Sulfuric Acid	Gold Etch – Type TFA
Hydrochloric Acid (38%)	Buffered Oxide Etch, 7:1 with Surfactant
Hydrogen Peroxide (30%)	Buffered Oxide Etch, 10:1 with Surfactant
Hydrofluoric Acid (48%)	Cr etchant(1020)
Alumina etchant	Tantalum etchant

### Chemical list for Base

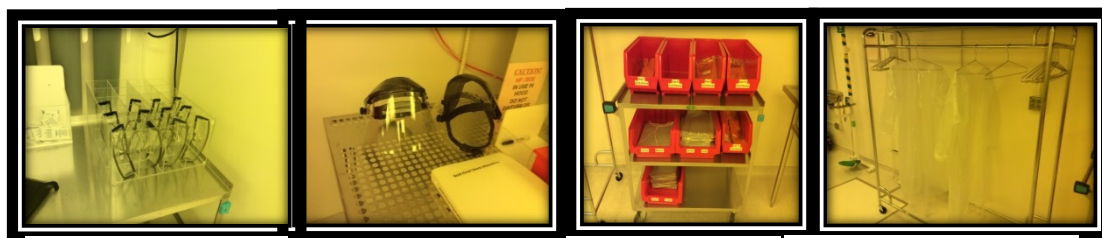
KOH	

- 2) All users must have formal lab safety training. Pitt EH&S offers Chemical hygiene, hazard communication and chemical specific trainings via their online training page. Information is available at the following link, <https://www.ehs.pitt.edu/training>. The Principle Investigator must maintain a copy of the training including the description of the training and training records complete with the list of those trained.
- 3) The chemicals for use are locked under the acid bench. The key to the lock can be retrieved from the lock box



in the pass through near the gowning room. The combination is 1,3,5,8. It is the responsibility of the user to secure the chemicals under the acid bench and return the key to the lock box. All chemicals should be locked when not in use.

- 4) Log into FOM. The facilities for the bench are locked and will not turn on until you are logged in. If the bench does not activate, simply log out and log back in.
  
- 5) Do all PPE before beginning to operate the bench. Goggles, Face Shield, Chemical gloves and sleeved aprons must be worn at all times while working at the hood. Make certain the PPE is in good condition. Do not use PPE if there are rips, tears or any holes. Any damaged PPE should be immediately discarded. If required PPE is empty or in low supply notify NFCF staff immediately.



Glasses

Acid Gloves

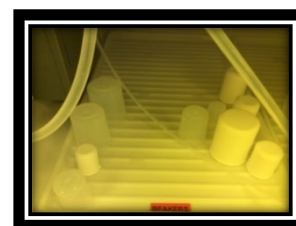
Aprons

- 6) The use of the bench is to be during daytime operating hours (9:00AM to 5:00PM).
  
- 7) A second person is allowed inside the working area to assist. This support individual must be acid safety trained, trained on the use of the bench and be dressed in the appropriate PPE. If the second person will be actively working with acids, they are required to wear all appropriate PPE per NFCF guidelines for acid work.
  
- 8) An individual can be designated a general buddy if this second person will not be inside the working area or actively working with any of the chemicals at the acid hood. The general buddy will be in the immediate

cleanroom area to provide assistance in the event of a chemical exposure or spill. A general buddy will be required to wear appropriate PPE for the cleanroom area they are working in.

- 9) The general buddy must be provided with information on the exact chemical or chemicals that the acid hood user will be working with during their period of time as a general buddy. The availability and location of safety data sheets (SDS) and PPE must be provided to the general buddy prior to work beginning in the acid hood.

- 10) Select appropriate and compatible lab ware for the desired process chemicals. **Remember HF must be placed only in the Teflon containers, and must use Plastic tweezers as well.**



Teflon Lab Ware

Remember KOH is not compatible with metal so do not use metal tweezers for KOH.



Calcium Gluconate Location

- 11) Note the location and availability of the Calcium Gluconate gel. Calcium Gluconate is used to coat skin exposed to HF acid. This can prevent or reduce damage to the body. This bench is approved for use of Buffered Oxide Etch (BOE). The BOE comprises of a 10:1 volume ratio of approximately 36%  $\text{NH}_4\text{F}$  to 4% HF, with the balance being distilled water. The general buddy must be provided information by NFCF staff personnel or the trained acid hood user on the location of Calcium Gluconate gel.

- 12) Note the location of the emergency shower and eyewash to the left of the acid bench. In the event of exposure, any affected area must be rinsed as quickly as possible and for at least 20 minutes. Upon activation of the eyewash or safety shower, emergency response (Pitt Police 412-624-2121) must be called to initiate medical attention.



**Emergency Shower**

- 13) In the event of an exposure that requires the use of the emergency safety shower or eyewash, the general buddy should provide immediate assistance to the acid hood user. Pitt Police (412-624-2121) should be called immediately once an acid exposure has been identified and treatment has begun.

- 14) If HF exposure has occurred, rinse the affected area for 20 minutes, use nitrile exam gloves and a tongue depressor to apply the Calcium Gluconate. Calcium Gluconate is to be used on skin only. Even after applying the calcium gluconate, a medical evaluation is essential and required.



**Calcium Gluconate**

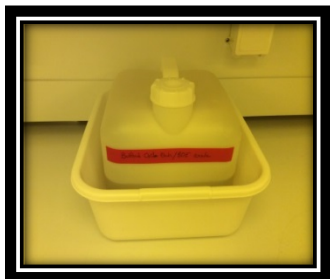
Refer to the response procedure outlined in University Guideline for HF (EH&SO4-010) for more details. A copy is located online and in the three ring binders located at the acid hood.

- 15) In the event of a hydrofluoric acid or BOE exposure, the general buddy should provide immediate assistance to the acid hood user. Pitt Police (412-624-2121) should be called immediately once an acid exposure has been identified and treatment has begun.
- 16) Two trained people must be present at all times when using the acid hood. One of the two individuals can be the designated general buddy that will be working in the immediate cleanroom area, but not at the acid hood.
- 17) Chemicals(acids + peroxide) must be used inside the Certified Chemical hood only. No chemicals are to be opened or poured outside of the exhausted and shielded area. KOH solutions and waste bottles are located in the trays of the caustic rack beside (outside of the hood).
- 18) Chemicals must be poured using two hands to allow stability and poured away from the user toward the rear of the hood.
- 19) Always cover your beaker with a watch glass when process reactions are occurring; reaction beakers should have a venting spout when covered with a watch glass
- 20) Always add acids or caustics to water, never water to acids or caustics and do it slowly to control and minimize any reaction.
- 21) NEVER MIX ANY ACID WITH CAUSTIC!



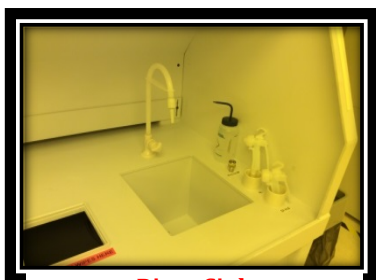
- 22) Any chemicals transported outside the acid hood must be double contained.
- 23) Absolutely no solvents are allowed inside the acid hood.
- 24) Once the process reaction has completely stopped and the liquid has cooled to room temperature, all waste chemicals must be disposed of into the designated, labeled waste containers. They contain the marble chips submerged in water for neutralization of the acids to prepare them for disposal.
- 25) Make certain to dispose of the correct chemicals into the correct waste container.

- 26) Slowly pour the waste liquid into the correct waste container. If a reaction begins to occur from the neutralization, stop pouring until the reaction slows. Continue to pour the remaining liquid into the waste container.



**Acid Waste Container**

- 27) Rinse the container with DI water and pour the residue into the waste container.



**Rinse Sink**

- 28) The lab ware can now be fully rinsed in the sink. Place it under the faucet and allow the running water to flow over the top for 15 minutes. For KOH, rinse water for 5 mins.

- 29) Notify the NFCF staff if any waste containers are over half full so that they can be removed and a new container placed in the bench.
- 30) All surfaces must be rinsed and wiped down after use. Dispose of the dirty wipes and contaminated PPE in the appropriate designated solid acid waste container located below the drop hole under the bench.
- 31) Lock the chemicals into the bench and return the key to the gowning room.
- 32) Log out of FOM.

## Piranha Etch Operation Procedure

Piranha etch is used to remove organic residue from substrates. The standard acid piranha is a 3:1 mixture of sulfuric acid with hydrogen peroxide. It is a self-starting reaction and extremely exothermic. Meaning it becomes extremely hot when the hydrogen peroxide is mixed with the sulfuric acid.

- 1) All users must read and understand the SDS documents for all chemicals listed for use in the Acid hood whether they are to use them or not. This information gives you details of the hazards and what can happen if an accident occurs. All SDS documents for the chemicals allowed in the acid bench are located in the three ring binder located at the bench.
- 2) Two trained people must be present at all times when working with Piranha Etch. Time can be scheduled for an NFCF staff member to be the second person present during regular NFCF staff working hours. One of the two individual can be the designated general buddy that will be working in the immediate cleanroom area, but not at the acid hood.
- 3) Don all PPE, including apron, acid gloves, eye goggles and face shield. The PPE is located next to the acid bench. Any damaged PPE should be immediately discarded. If required PPE is missing NFCF staff must be immediately notified. Do NOT prepare Piranha solution without wearing all aforementioned PPE.
- 4) Test gloves by inflating gently and rolling the cuff down to insure they are leak free. Gloves can be used for piranha for only a single day.

- 5) Use only Pyrex beakers for mixing the piranha solution. Before adding the chemical, label the container with a piece of red clean room tape with the chemical clearly stated in black sharpie on the tape. This label is important to allow the mixture to sit overnight in the back of the bench for the solution to completely stop reacting and cool. The contents of all lab ware must be known at all times.
- 6) During the preparation of the mixture for the etching process, always add the hydrogen peroxide to the sulfuric acid. Note: If the H<sub>2</sub>O<sub>2</sub> concentration becomes higher than 50% an explosion can occur due to the amount of hydrogen gas that can be produced from the reaction.
- 7) Carefully measure the amounts of the mixture and mix the chemicals slowly in order to control the reaction intensity.
- 8) Prepare only the amount of mixture that is needed for the process. Excess liquid creates unnecessary waste to dispose of and can result in larger spills and increased chance of chemical exposure as the result of an accident.
- 9) The reaction is energetic and will become hot. It can reach temperatures in excess of 100 °C.
- 10) Warning! Adding any acids, or bases such as photo resist can accelerate the reaction.
- 11) Substrates should be rinsed and fully dried before placing them in the piranha bath.
- 12) Leave the hot piranha solution in the reaction beaker and cover it with a watch glass to control any

splatter; the beaker should have a spout so that the reaction can properly vent.

- 13) Once the piranha solution has reached room temperature and shows no sign of a continued reaction it can be disposed of into the dedicated waste container. The piranha solution must sit overnight prior to this disposal.
- 14) As stated above, any container with chemicals that is left in the bench must be labeled using a piece of red clean room tape with the chemical clearly stated in black sharpie on the tape.
- 15) Remove the tape label from the beaker. Beakers and tools are to be thoroughly rinsed with DI water.
- 16) Place fully rinsed lab ware on the dish washer cart for cleaning.
- 17) Never store piranha solution.
- 18) Do not mix organic solvents with piranha solution. Never add solvents such as acetone, IPA, photo resist or nylon to the mixture.
- 19) Carefully remove contaminated PPE and place it into the solid acid waste container labeled for wipes and PPE.

## Silicon Oxide Etch Operation Procedure

The Buffered Oxide Etch comprises of a 10:1 volume ratio of approximately 36%  $\text{NH}_4\text{F}$  to 4% HF, with the balance being distilled water. It is used to remove silicon oxide and create a fresh surface of silicon.

- 1) Before starting, make certain that you are familiar with the MSDS and all protocols for the use of the chemical. All users must read and understand the SDS documents for all chemicals listed for use in the Acid hood whether they are to use them or not. This information gives you details of the hazards and what can happen if an accident occurs. All SDS documents for the chemicals allowed in the acid bench are located in the three ring binder located at the bench
- 2) Remember that BOE contains HF. HF has unique hazards that must be noted. It is extremely dangerous in both a liquid and gaseous state. HF can cause burns that may take up to 24 hours to become visible or cause pain. HF is readily absorbed through the skin and will bind with the calcium and magnesium in your body to form insoluble salts. These salts interfere with cellular metabolism causing cellular necrosis and even death.
- 3) Know that BOE is not dilute HF. It is not any less dangerous.
- 4) Two trained people must be present at all times when working with Silicon Oxide Etch. Time can be scheduled for an NCF staff member to be the second person present during regular NCF staff working hours. One of the two individual can be the designated general buddy that will be working in the immediate cleanroom area, but not at the acid hood.

- 5) Don all PPE, including apron, acid gloves, eye goggles and face shield. The PPE is located next to the acid bench. The BOE solution is located under the bench. Any damaged PPE should be immediately discarded. If required PPE is missing NFCF staff must be immediately notified. Do NOT prepare Piranha solution without wearing all aforementioned PPE.
- 6) Test gloves by inflating gently and rolling the cuff down to insure they are leak free. Gloves are one time use only for any HF processes.
- 7) Safety:
  - a. Note the location and availability of the calcium gluconate gel when using any form of hydrofluoric acid.
  - b. Also, note the location of the safety shower and eyewash. If HF exposure has occurred, after rinsing the affected area, use nitrile exam gloves to apply Calcium Gluconate. Even after applying the calcium gluconate, a medical evaluation is essential.
  - c. Refer to the response procedure outlined in University Guideline for HF (EH&SO4-010) for more details. A copy is located online and in the three ring binder located at the acid hood.
  - d. University EH&S guidelines for HF use can be found at:  
<http://www.ehs.pitt.edu/assets/docs/hydrofluoric-acid.pdf>
- 8) Always use Teflon beakers, since this solution contains HF that will etch glass. Before adding the chemical, label the container with a piece of white clean room tape with the chemical clearly stated in black sharpie on the tape. This label is important to allow the mixture to sit overnight in the back of the

bench for the solution to completely stop reacting and cool. The contents of all lab ware must be known at all times.

- 9) Use only the amount of BOE that is needed for the process. Excess liquid creates unnecessary waste to dispose of and can result in larger spills in the result of an accident.
- 10) Use Teflon or other HF compatible tweezers when transferring sample.
- 11) Buffered Oxide Etch (BOE) waste must be transferred into the dedicated waste container. Do not place the waste into any glass container for the Piranha etch since the HF will attack the glass.
- 12) Remove all label tape from the lab ware. Beakers and tools are to be thoroughly rinsed with DI water.
- 13) Place fully rinsed lab ware on the dish washer cart for cleaning.
- 14) All contaminated PPE and wipes are to be placed into the designated solid acid waste container.



## Cr etching for photomask

After write mask on MLA100, follow the following procedures for making photomask:

1. Develop for 1 min in AZ400K:DI (1:4 ratio) for 1 min with minimal agitation
2. Rinse thoroughly in DI water and blow dry with N2 spray gun
3. Inspect with optical microscope
4. O2 descum in RIE (500mT, 50W, flow 50sccm, time 20s)
5. Etch Cr in Transene Chromium Etchant 1020 until clear (typically about 180sec)
6. Rinse thoroughly in DI water and blow dry with N2 spray gun
7. Inspect with optical microscope (if residual Cr remains, repeat steps 5-7 as needed, with small time increments of 15-60sec for Cr etch)
8. Strip remaining resist from mask in Microposit 1165 heated to 50C
9. Rinse thoroughly in IPA and blow dry with N2 spray gun
10. Inspect in optical microscope for residual resist or defects

Cr etchant 1020 (1020AC) is located in the acid cabinet. Notify NCF staff one day before you will use it.

### **Guideline for safe use of Nitric Acid**

Nitric Acid (**HNO<sub>3</sub>**) is a clear, colorless to slightly yellow inorganic acid. In concentrations above 70%, nitric acid is called "fuming" or "red fuming." The material is not combustible, however it is a strong oxidizer and care should be taken in storing it away from incompatibles (see below). Spontaneous ignition or combustion takes place when a substance reaches its ignition temperature without the application of external heat.<sup>1</sup> Materials susceptible to spontaneous combustion due to contact with nitric acid include oily rags, dust accumulations, and many organic materials. Routes of entry to the body include inhalation and ingestion. Skin contact results in severe irritation and burns. Nitric acid is not listed as a carcinogen.

### **Health Hazards**

1. Symptoms of overexposure include irritation and/or burning of the affected area.
2. Inhalation burns are serious and require immediate medical attention.
3. Ingestion causes abdominal pain, vomiting, hemorrhaging, and organ perforation. If the acid is ingested, drink copious amounts of water and seek medical attention. Do not induce vomiting.
4. If acid is spilled onto the body, wash the acid off with generous amounts of water for 15 min.
5. Spills which occur over a large body surface require the use of the nearest emergency shower and removal of contaminated clothing.
6. Eye wash locations should be easily accessible in case of eye contact. Flush eyes for a minimum of 15 minutes and notify the Campus Police and the EH&S office immediately.

## **Safety Precautions for Nitric Acid Use**

1. All University of Pittsburgh staff, students and employees who work in labs containing nitric acid should familiarize themselves with the unique dangers and special precautions that need to be taken when handling nitric acid.
2. Incompatibles include flammables, bases, hydrogen sulfide, organic materials, metals and metal compounds.
3. Work with nitric acid should always be performed in a chemical fume hood. Care should be taken to clear the hood of organics, flammables, and other incompatibles.
4. Personal protective equipment including the appropriate gloves, safety glasses, and lab coat or apron must be worn.
5. OSHA Permissible Expose Limit (PEL)- 2 ppm
6. Immediately Dangerous to Life and Health (IDLH)- At levels greater than or equal to 25ppm

## Storage, Spills and Waste Issues

1. As a result of its wide range of incompatible chemicals, nitric acid is difficult to keep safely in storage. Ideally, nitric acid should be stored in its own acid cabinet. However due to space considerations this is not always possible. The next best place for storage is with other inorganic acids and within secondary containment.
2. Nitric acid spills are serious and care should be taken to follow all chemical spill clean up procedures.
3. Small or dilute concentrations (10 ml of >50% or 100 ml of dilute) can be cleaned up using a spill kit. The entire spill kit containing the clean up materials can then be labeled and placed in a satellite accumulation area for pickup and disposal.
4. If large amounts of acid are spilled, or if the spill is beyond your ability and training to clean up, evacuate the laboratory and contact EH&S or the University Police from a safe location.
5. Never pour waste nitric acid into a sink or sewer drain.

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<sup>1</sup> Committee on Hazardous Substances in the Laboratory, Assembly of Mathematical and Physical Sciences, National Research Council. *Prudent Practices for Handling Hazardous Chemicals in Laboratories*. 1981. pp. 59.

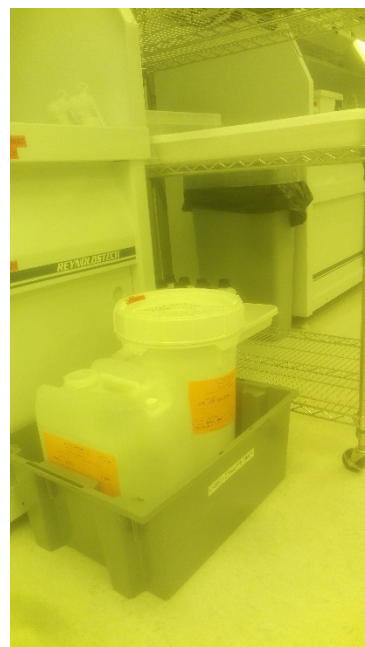
## KOH operation procedures

KOH solution is mainly used to etch silicon substrates. It is corrosive and can burn skin very seriously. All the stuff related to KOH etching are located on the rack beside the acid hood.

- 1) All users must read and understand the MSDS documents for all chemicals listed for use. This information gives you details of the hazards and what can happen if an accident occurs. All MSDS documents for the chemicals allowed in the acid bench are located in the three ring binder located at the bench.
- 2) Do all PPE, including apron, acid gloves, eye goggles and face shield. The PPE is located face to the acid bench. Any damaged PPE should be immediately discarded. If required PPE is missing NCF staff must be immediately notified. Do NOT prepare KOH solution without wearing all aforementioned PPE.
- 3) Test gloves by inflating gently and rolling the cuff down to insure they are leak free. Gloves can be used for KOH for only a single day.
- 4) All the caustic stuff are located on the caustic rack. Use only Pyrex beakers for mixing the KOH solution. Before adding the chemical, label the container with a piece of red clean room tape with the chemical clearly stated in black sharpie on the tape. This label is important to allow the mixture to sit overnight in the back of the bench for the solution to completely stop reacting and cool. The contents of all lab ware must be known at all times.



- 5) During the preparation of the mixture for the etching process, always add KOH solution to DI water slowly. Mixing of KOH and water will create heat.
- 6) Carefully measure the amounts of the mixture and mix the chemicals slowly in order to control the reaction intensity.
- 7) Prepare only the amount of mixture that is needed for the process. Excess liquid creates unnecessary waste to dispose of and can result in larger spills and increased chance of chemical exposure as the result of an accident.
- 8) Substrates should be rinsed and fully dried before placing them in the bath.
- 9) Leave the hot solution in the reaction beaker and cover it with a watch glass to control any splatter; the beaker should have a spout so that the reaction can properly vent.
- 10) Once the KOH solution has reached room temperature and shows no sign of a continued reaction it can be disposed of into the dedicated waste container. Pull out the caustic rack and place the waste tray close to the hood for waste dumping.
- 11) Clean all the beakers and funnel with flush DI water for 5 mins. Dry them with wipes after clean done.
- 12) Remove the tape label from the beaker. Place used lab ware on the dish washer cart for cleaning.
- 13) Do not mix caustic solvents with any acids and solvents.



Carefully remove contaminated PPE and place it into the designated waste containers on the caustic rack.