

Piranha SOP

Summary

- Piranha is a strong oxidant and is extremely corrosive. Use only if necessary. Consult with PI or senior lab investigators before you use piranha for the first time.
- Explosive hazard: strong oxidizers can react violent with organic materials.
- Follow outlined disposal instructions.

What is Piranha?




Piranha, or piranha etch, is a strong oxidant that is generated from a 3:1 mixture of concentrated sulfuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2). It is most often used to remove organic residues from substrates, and is common in microfabrication and microelectronics laboratories. Piranha will hydroxylate surfaces by adding an $-OH$ group to make them hydrophilic, which also makes it good at decontaminating glassware.



Mixing sulfuric acid and hydrogen peroxide results in an exothermic reaction. Never use Piranha that is still boiling or very hot. When the solution has cooled, it can be moderately heated to sustain its reactivity. The warm solution cleans organic compounds off substrates and oxidizes or hydroxylates glass surfaces. Cleaning usually requires about 10 to 40 minutes, after which the substrates can be removed from the solution.

Any work with this chemical should follow proper guidelines as laid out in this SOP including proper hazard mitigation procedures and required personal protective equipment. Please consult with PI or senior lab investigators before you use piranha for the first time.

Hazards

	Piranha solution is extremely corrosive to organic material. Direct contact will burn skin and be extremely corrosive to mucous membranes, upper respiratory tract and eyes. Both liquid and vapor phases are extremely corrosive to skin and respiratory tract.
	Piranha Solution is a very strong oxidizer when in contact with organic compounds.
	Piranha solution is extremely energetic and exothermic, which may result in explosion if not handled carefully. Solutions made using hydrogen peroxide at concentrations greater than 50% may cause an explosion. Dissolving a large amount of organic contaminant will cause violent bubbling and a release of gas that can cause an explosion.

Corrosive Hazards

This solution contains highly corrosive sulfuric acid, and can easily damage eyes, or dissolve fabric and skin causing severe chemical burns in the process. The solution is extremely poisonous if ingested.

In addition, the vapors emitted from boiling piranha can cause severe burns to the respiratory tract if inhaled. Always work with piranha in a fume hood, with the sash as low as possible. Ensure the face velocity of the air entering the fume hood is appropriate by checking the flow controller before beginning work. Report any issues with fume hoods to the Solutions Center: <https://www.umass.edu/af-forms/physicalplant/service-request>.

Fire/explosion

- **ALWAYS SLOWLY** add the hydrogen peroxide to the acid, never vice versa. The hydrogen peroxide concentration should never exceed 50%, or the solution may explode.
- Mix the solution carefully. The dissolution of sulfuric acid in the largely aqueous hydrogen peroxide solution is highly exothermic and can produce flash boiling. The solution also evolves oxygen that can exacerbate bumping. Use an ice bath if necessary to control temperature.
- **NEVER** use piranha to clean grossly contaminated surfaces. Piranha should only be used to remove trace contaminants or to treat clean glass.
- Hot piranha solution can react rapidly. Use with caution.
- **NEVER** dispose in the same container as organic solvents or store in a closed container. The mixture may explode. Use a pressure venting cap for waste containers.
- DO NOT store wash bottles with organic compounds on the same shelf or bench as the piranha solution. The compounds may react and explode or combust.

What Activities Pose a Risk?

Activities that pose a risk include:

- Using the material with larger quantities of organic materials
- Using piranha solutions with higher concentrations of peroxide
- Using large volumes of piranha
- Storing piranha solutions in closed containers

How to Minimize Exposures

When working with any hazardous material or process, always conduct a thorough risk assessment and employ the hierarchy of controls to minimize risk. Specific applications of the hierarchy of controls to the unique hazards of Piranha are listed below. Apply the controls in the order of most effective to least effective (see graphic at right), and apply as many controls as possible to reduce the risk to the lowest achievable level.

Elimination/Substitution

- Only use piranha when necessary. Consider alternative etching and cleaning solutions that are less hazardous than Piranha.

Engineering Controls

- Generate and handle Piranha in a working fume hood with the sash separating yourself from the material.
- Work with the sash as low as possible and never raise it above the indicated sash limit.
- Keep the space decluttered. Hot plates or electronics that are in the fume hood and not in use can impede air flow.

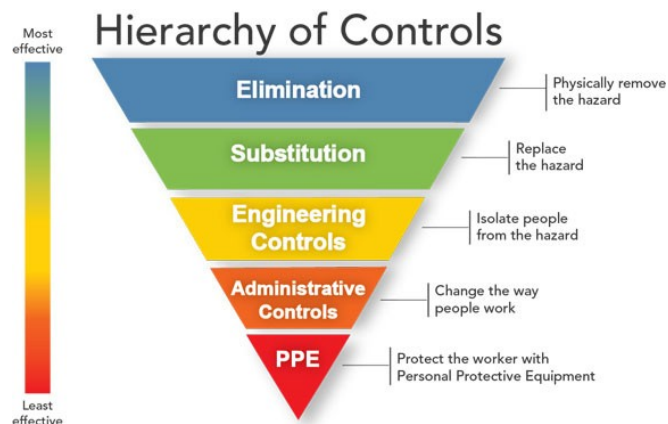
Administrative Controls

- Before use:
 - Consult the manufacturer's Safety Data Sheet and additional chemical information at <https://cems.unh.edu/umass/CEMS/SearchSDS>
 - Locate nearest eyewash and shower and confirm that they are accessible and within 50 ft. of the work area.
 - Ensure all glassware is in good working order, do not use any cracked, chipped, or otherwise damaged equipment.
- Clearly label each container used to house piranha with a warning sign that indicates the solution's name, corrosive and explosive hazards, and contact information for the individual who generated it.
- Do not transport the solution around the room in beakers or other open containers that may spill easily.
- Only handle Piranha while others are present in case of emergency.
- Do not tightly cap a vessel with piranha, unless it is a ventilated cap and the solution is cool.
- Only use glass containers to house the solution. Piranha may melt or deteriorate plastic.
- Piranha must be prepared fresh before each use to ensure efficacy. Only prepare the amount needed for the procedure and only work on a small scale (i.e., 100 mL or less).
- Piranha becomes hot when mixing. Avoid handling containers of freshly prepared reagent when possible. Use tongs or hot mitts to handle containers when necessary.

Personal Protective Equipment

Always wear the following PPE while handling Piranha:

- Lab coat, close-toed shoes, full pants;
- Safety glasses (preferably chemical splash goggles);
- Exam-style nitrile gloves **UNDERNEATH** acid-resistant gloves with extended cuffs.
 - These gloves should be rubber, butyl, neoprene, or Viton. Nitrile gloves will not provide appropriate protection.
- A face shield is required when handling quantities greater than 100 mL



Waste Handling

Used Piranha should be treated as hazardous and disposed of properly. Used solutions should be allowed to cool and degas fully before disposal of waste. Waste should be stored until pickup in a glass bottle, appropriately labeled, with a pressure venting cap. Piranha should be disposed of alone with its own dedicated container; never put solution into a waste container with other materials, as a violent reaction could occur. The spent solution should still be considered an oxidizer, and therefore the waste should not be stored in the same secondary container as incompatible (e.g. organics, bases) waste.

Additions to the waste container should be performed in the fume hood. Following each addition to the container, the contents of the piranha waste bottle must be carefully swirled to achieve agitation. Make sure that the bottle is open while swirling. Consider documenting additions to the container to keep track of any potential adverse reactions. Print off the sheet at the end of this document for your lab, and record each time Piranha is added to the designated waste bottle. In addition to noting the time and date, personnel performing the agitation should take note of either heat or gas evolved after swirling. If there is gas evolution, note under the column 'Swirled' as 'gas evolution'. After a minimum of 48 hours, the contents should again be swirled and the action documented. Always keep the piranha waste bottle in a clear, uncluttered area of a hood.

To have the waste picked up by EH&S staff, request removal through CEMS at <https://cems.unh.edu/umass/CEMS/RequestRemoval>.

Emergency Procedures

In the event of a spill involving piranha contained in a hood, it should be safe for lab personnel to clean up following the general procedure for small spills detailed in the University's Chemical Hygiene Plan. People nearby should be alerted to the spill. PPE should be worn while cleaning the spill. Use acid spill neutralizer such as sodium bicarbonate, collect residue using absorbent material, and label and dispose of as hazardous waste. For larger spills or spills outside the fume hood, the area should be evacuated (with the emergency exhaust/purge pushed if safe and present) and EH&S should be immediately called (413-545-2682). If you ever feel unsafe cleaning up a small spill, feel free to contact EH&S.

Exposures to hazardous materials should follow the general procedures for exposures outlined in the University's Chemical Hygiene Plan.

For a major exposure requiring the use of a drench shower or eye wash:

- Have someone call 911 (report the building name, room number, and street address) or 413- 545-3111 (or simply 5-3111 from a campus line) to report the incident and request medical help. If possible, communicate to the first responders the nature of the exposure.
- Help the affected individual to position their head over the eyewash and activate it, or position them under the drench shower and activate it as appropriate.
 - Always ensure your own safety before helping others. Only help if it is safe for you to do so.
 - Wear gloves, safety glasses, and a lab coat.
- If using an eyewash: Instruct the affected individual to open their eyes and roll them around while the water is flowing. Help them to hold their eyes

open if necessary and safe to do so.

- If using a drench shower: Remove all clothing from the affected area while under the shower.
- Flush the affected area for 15 minutes with water.

For minor exposures such as a spill to readily accessible extremities (e.g. hand)

- Flush the affected area in a sink equipped with potable water for at least 15 minutes.
- Go to University Health Services (UHS) for medical evaluation, and tell them you have had a lab exposure.
- Notify EH&S (413-545-2682) as soon as possible and complete the lab incident form (<https://ehs.umass.edu/lab-incidents-and-lab-incident-report-form>).

Sources

EHS Harvard SOP –

https://www.ehs.harvard.edu/sites/default/files/lab_safety_guideline_piranha_etch.pdf

EHS University of Colorado Boulder SOP – <https://ehs.colorado.edu/wp-content/uploads/2015/06/Use-and-Disposal-of-Acidic-Piranha-Solutions-04.23.14.pdf>

General Information/Overview (Wikipedia) – https://en.wikipedia.org/wiki/Piranha_solution

Piranha Safety Data Sheet: ComStar –

https://www.globalindustrial.com/site/images/Comstar15/Piranha_SDS.pdf

