HARVARD
Campus Services
ENVIRONMENTAL HEALTH & SAFETY

Laboratory Safety Guideline

Piranha Solution

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Overview

This document outlines minimum expectations for use of piranha solutions in Harvard labs. Departments or labs may choose to implement more stringent requirements for those operating in their spaces.

Piranha solution, also known as piranha etch, is a strong oxidizing agent that removes most organic matter. It will also hydroxylate most surfaces by adding hydroxyl (-OH) groups, rendering them highly hydrophilic (water compatible). Piranha solutions are often used to clean organic residues off substrates.

There are two types of piranha solutions:

- Acid piranha solutions are a mixture of sulfuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2). Typically, it is made as a 3 to 1 mixture of concentrated sulfuric acid with 30% hydrogen peroxide.
- Base piranha solutions are a mixture of ammonium hydroxide (NH_4OH) and hydrogen peroxide. Typically, it is made as a 3 to 1 mixture of ammonium hydroxide with 30% hydrogen peroxide.

Both types of piranha solutions are equally dangerous once the components begin to react with each other. The reaction in acid piranha solutions is self-starting, while base piranha solutions must be heated to 60^{o}C before the reaction begins.

Hazards

The individual chemicals used to make piranha solutions and the mixture itself are hazardous. Additional chemicals used in combination with piranha solutions must also be assessed prior to work. Review the Safety Data Sheet (SDS) for any chemical used in combination with piranha solutions.

Hazard Symbol	Hazard Description
	The reaction of hydrogen peroxide with either sulfuric acid or ammonium hydroxide can be extremely energetic and exothermic, which may result in an 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 contaminants will cause violent bubbling and a release of gas that can cause an explosion.
	Both sulfuric acid and ammonium hydroxide are corrosive and can cause severe skin burns and eye damage. Piranha solution is extremely corrosive to organic material. Direct contact will burn skin and is extremely corrosive to mucous membranes, upper respiratory tract, and eyes. Both liquid and vapor phases are extremely corrosive to skin and respiratory tract.
	Hydrogen peroxide is a strong oxidizer. Piranha solution is a very strong oxidizer when in contact with organic compounds.

Training

Lab personnel working with piranha solution must complete applicable Environmental Health and Safety (EH&S) training and keep it up to date. At a minimum, this includes the following trainings:

- General Lab Safety: Renewed annually.

- Laboratory Safety Orientation Checklist: Completed for each lab a person works in and kept on file by the lab.

In addition, piranha solution users and those working in spaces where this mixture is used should review this document and be familiar with emergency procedures.

Precautions

Personal Protective Equipment

Proper Personal Protective Equipment (PPE) and attire are important whenever working with hazardous chemicals. Each space should have a lab-specific PPE Assessment posted for reference by lab users.

The following table outlines basic requirements when handling piranha solutions. More information can be found on the EH&S Lab PPE webpage.

PPE Type	Requirement
Attire	Wear a combination of clothing and shoes that fully cover the legs and feet.
Eye and Face Protection	Wear safety glasses with side shields at a minimum. Use safety goggles when there is a greater risk of splashes and for spill cleanup. A face shield over safety goggles may be needed when working with larger volumes or where there is a greater splash risk.

PPE Type	Requirement
Gloves	Wear compatible chemically resistant gloves when handling potentially hazardous chemicals. At a minimum wear rubber, butyl, neoprene, or viton gloves. Regular nitrile disposable gloves will not provide appropriate protection. For spill cleanup, work with larger volumes, or where there is a greater splash hazard, wear gloves with extended cuffs. Recommended gloves include Ansell Microflex 93-260 (combination nitrile and neoprene), Ansell AlphaTec Solvex 37-175 (nitrile), and Ansell AlphaTec 38-514 (butyl polymer). Glove compatibility with other chemicals used in combination with piranha solutions must also be considered. Refer to each chemical's SDS and the EH&S Lab Glove Selection Guide for help identifying compatible gloves.
Lab Coat	Lab coats are required when handling piranha solution, such as when carrying bottles or hazardous waste to a mini-main accumulation area. Acid-resistant aprons are required when handling large quantities outside of the fume hood (>500mL) or where splashing is more likely.
Respiratory Protection	Respiratory protection should not be needed if using engineering controls such as fume hoods or local exhaust ventilation. If work with piranha solutions is conducted without engineering controls, contact EH&S for an assessment.

General Precautions

- Always add hydrogen peroxide to the acid or base very slowly, never vice versa.
- Hydrogen peroxide stock concentrations should be kept below 30% and should never exceed 50%.
- Always use glass containers, preferably Pyrex. Piranha solution will melt plastic.

- Piranha solution should be made up as needed and used fresh due to the self-decomposition of hydrogen peroxide. Do not maintain a stock solution of the piranha mixture.
- Prepare small amounts of solution to be used for each application.
- Piranha solutions, as well as any corrosive or hazardous substances, should preferably only be used during operational hours, 9:00 am to 5:00 pm, Monday through Friday. Please have a second person present if working with piranha solutions after hours.
- Do not store wash bottles containing organic compounds such as acetone or isopropyl alcohol on the same work surface as the piranha solution.

Before Starting Work

- Determine if a less hazardous material can be used instead of piranha solution
- Try more stable methods of removing stains, tars, or clogs before using piranha solution for those purposes.
- Ensure that a written Standard Operating Procedure (SOP) including safety information is available. More information on lab-specific SOP requirements can be found in Part III of the Harvard University Chemical Hygiene Plan.
- Review the manufacturer's SDS and additional chemical safety information available on the EH&S website.
- Be familiar with the general University emergency procedures in the EH&S Lab Emergency Response Guide.
- Identify the location of the nearest eyewash and safety shower and verify that they are accessible.
- Locate and verify that appropriate piranha solution spill cleanup materials and neutralizers are available. These should include the following items:
    - Acid neutralizer if using acid piranha solutions.
    - Alkaline neutralizer if using base piranha solutions.
    - Scraper.

  - pH test strips.
  - Disposable scoop pan.
  - Polystyrene bag or 1 gallon mayo-style jar for waste collection.
- Clear fume hood of all excess materials and equipment not needed for procedure. Piranha solution is extremely corrosive and could damage equipment kept in the hood. It also reacts with many other chemicals.
- Substrates should be cleaned, rinsed and dried before being placed in a piranha bath.

During Work

- **Avoid inhaling piranha solutions!**
  - Perform all experimental operations within a fume hood or other approved ventilated enclosure.
  - All handling of hot piranha solution must be done with clean glassware within a fume hood.
  - Work with the sash as low as possible and never raise it above the indicated sash limit.
  - Never remove hot piranha solution from the fume hood.
- **Avoid any contact with piranha solutions!** Wear PPE as outlined in the Personal Protective Equipment section.
- Always work behind the fume hood sash and wear a face shield if the fume hood sash must be open higher than 18 inches from the base.
- Wash hands and forearms thoroughly with soap and water each time gloves are removed.
- Be aware of potential incompatibilities, such as acids, bases, or organic materials such as acetone and isopropyl alcohol.
- Use materials and containers appropriate for piranha solutions such as glass, preferably Pyrex.

- Mix the solution in a fume hood with the sash down as low as possible. The solution may be mixed before application or directly applied to the material. If directly applied to the material, add the sulfuric acid or ammonium hydroxide first, followed by the hydrogen peroxide.
- Piranha solution should never be left unattended if hot.
- Never seal containers containing piranha solution. Avoid using airtight containers as pressure can build up inside from the self-decomposition of hydrogen peroxide and oxidation products of organic compounds. Vented caps are available from EH&S through the Chemical Waste Pickup and Services form.
- Mixing hot piranha solution with organic compounds may cause an explosion. Organic compounds include but aren't limited to acetone, photoresist, isopropyl alcohol, other organic solvents, and nylon.
- Containers used with piranha solution must be very clearly labeled and a warning sign, visible to any user working under the same fume hood, must be posted to indicate the working piranha solution, corrosive and explosive hazards, and contact information of the person responsible for the container.
- The reaction of hydrogen peroxide with sulfuric acid or ammonium hydroxide is very energetic and potentially explosive. Once the reaction begins the solution is very likely to become hot, exceeding 100°C. Handle with care. Picking up a beaker that is hot will be very painful, may melt gloves, and lead to a spill.
- Do not transport piranha solutions around the room in beakers.
- Never pour chemicals back into the original container.
- Immersing a substrate into piranha solution should be done slowly to prevent thermal shock that may crack the substrate material.

After Completing Work

- Clean work area.
- **Do not store piranha solutions!** Oxygen released from self-decomposition and oxidation byproducts of organic compounds can cause the container to over pressurize and explode. Always mix a fresh solution.
- Piranha solution waste requires special handling.

- Leave the hot piranha solution in an open container in a fume hood or ventilated enclosure until cooled.
- Put the waste solution in a cleaned and dried container with a vented cap. Request vented caps from the Chemical Waste Pickup Services Online Request. If a vented cap is unobtainable, screw a regular cap on lightly to allow pressure relief and prevent over pressurization.
- Label the container with a properly filled out hazardous waste tag. Check off Oxidizer and Corrosive as the hazards on the tag.
- Place the appropriately closed and labeled waste container into a secondary containment bin, segregated from organic chemical waste.
- Place a label on the container declaring that no other chemical waste streams should be added. Do not mix with organic waste compounds such as acetone, methanol, or isopropanol. Do not add any acids or bases to the solution once completed.
- Submit a pickup request using the Chemical Waste Pickup Services Online Request form.

- Return other chemicals to appropriate storage following the Lab Chemical Storage Guide.
- Wash hands and forearms thoroughly with soap and water before leaving the lab.

Emergency Procedures

- Refer to the Lab Emergency Response Guide and the information outlined in this section.
- Notify PI or supervisor of any exposures or incidents involving piranha solution. The PI or their designee must report all exposures or injuries within 24 hours.

First Aid

Any exposure to piranha solution must be responded to immediately to reduce injury. Enlist the help of nearby lab members following exposure to assist with decontamination and medical follow-up. Responders must don appropriate PPE and collect any contaminated clothing or shoes as hazardous waste.

Skin Contact

Treatment starts immediately following exposure. The solution may cause skin burns.

- Remove all potentially contaminated clothing and jewelry and treat as hazardous waste.
- Flush affected skin area using sink if on hands or arms or using a safety shower for 15 minutes.
- Seek medical follow-up. Call 911 for major skin exposure.

Eye Contact

Solution is corrosive and irritating to eyes.

- Rinse eyes at an eyewash station for at least 15 minutes.
- Seek medical attention.

Inhalation

- Move person to a location with fresh air.
- Seek medical attention.

Ingestion

- Solution may irritate the respiratory tract.
- Conscious persons should be assisted to an area with fresh, uncontaminated air.
- Seek medical attention. Call 911 in the event of respiratory irritation, cough, or tightness in the chest. Symptoms may be delayed.

Sharps Injury

- Immediately wash the area with soap and water for at least 15 minutes.
- Seek medical assistance.

Spill Response

Spills outside fume hood or ventilated enclosure:

- Alert others of the spill.
- Evacuate to a safe distance and prevent entry.
- Contact the Operations Center by calling 617-495-5560. Harvard Medical School (HMS) and Harvard Dental School of Medicine (HSDM) labs should call 617-432-1901.
- Remain in a safe location until EH&S or other response personnel arrive.

Spill inside fume hood or ventilated enclosure less than 500 mL:

- A person may assist in the clean-up effort of small amounts of piranha solution if trained and comfortable.
- Wear PPE described above and use appropriate spill supplies.
- Use the acid neutralizing agent if acid piranha solution spilled or the alkaline neutralizer if base piranha solution spilled. Do not use combustible organic materials such as spill pads or paper towels to clean up the spill unless the spilled material has been properly neutralized and pH tested to a safe range of pH 6 to pH 8.
- Collect debris in appropriate container and move to the Satellite Accumulation Area (SAA).
- Label container with appropriately completed hazardous waste tag.
- Request a waste pickup.

Otherwise close the fume hood sash and contact the Operations Center by calling 617-495-5560. HMS and HSDM labs should call 617-432-1901.

Fire

- In the event of fire, evacuate and bar further entry.
- Activate the fire alarm and leave the building.

- Once at a safe location, call 911 to notify them of the nature of the alarm.

Supporting Documents

Harvard Resources

- Lab Chemical Storage Guide
- Lab Emergency Response Guide
- Lab Glove Selection Guide
- Lab Safety Guideline: Hydrogen Peroxide
- Lab PPE webpage
- Safe Chemical Work Practices

Outside References

- Boston University Photonics Center, P. Mak, Piranha Clean Procedure
- Oregon State University, Environmental Health & Safety, Safety Instruction: Piranha Solution
- UC Riverside, Generation, Use and Disposal of Piranha Solutions Standard Operating Procedure
- The University of Illinois at Urbana-Champaign, Division of Research Safety, Piranha Solutions
- University of Maryland, Laboratory for Advanced Materials Processing, J. Park and L. Henn-Lecordier, Standard Operating Procedure for Piranha Solutions, January 2003.
- Yale University, Environmental Health & Safety, Standard Operating Procedure Piranha Solution