

LABORATORY SAFETY GUIDELINE

Piranha Solution

Piranha Solution, also known as piranha etch, is a mixture of Sulfuric acid (H_2SO_4) and Hydrogen peroxide (H_2O_2) used to clean organic residues off substrates. The mixture is a strong oxidizing agent that removes most organic matter, and it will also hydroxylate most surfaces (add -OH groups), rendering them highly hydrophilic (water compatible). *Acid piranha* is a 3:1 mixture of concentrated Sulfuric acid with 30% hydrogen peroxide. Also used is the *base piranha*, a 3:1 mixture of Ammonium hydroxide (NH_4OH) with 30% hydrogen peroxide. Both are equally dangerous when hot, although the reaction in the acid piranha is self-starting whereas the base piranha must be heated to 60°C before the reaction takes off.

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.

PRECAUTIONS

Before Starting Work:

- Before using Piranha solution, more stable methods of removing stains, tars, or clogs should be attempted. Substrates should be cleaned, rinsed and dried before being placed in a piranha bath.
- Review manufacturer's Safety Data Sheet and additional chemical information at the [Harvard EH&S SDS Database](#).
- Ensure that a written standard operating procedure (SOP) including safety information is available.
- Ensure you are familiar with University emergency procedures in the [Lab Emergency Response Guide](#).
- Identify the location of the nearest eye wash and safety shower stations and verify they are accessible.
- Locate and verify that appropriate Piranha Solution spill cleanup materials and neutralizers are available.
 - Acid neutralizer (or alkaline neutralizer for base piranha solutions)
 - Scraper
 - pH test strips
 - Disposable scoop pan
 - Polystyrene bag for waste collection or mayo jar

When Preparing the Piranha Solution:

- ALWAYS add the hydrogen peroxide to the acid very slowly, never vice versa. Hydrogen peroxide concentrations should be kept below 30% and should never exceed 50%.
- Always use glass (preferably Pyrex) containers. Piranha solution will melt plastic. Piranha solution should be used freshly-prepared, 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 am to 5 pm, Monday through Friday). Please have a second person present if working with piranha after hours.
- Do not store wash bottles containing organic compounds on the same work surface as the piranha solution.

During Work:

- Mix the solution in a fume hood with the sash between you and the solution. The solution may be mixed before application or directly applied to the material, applying the Sulfuric acid first, followed by the 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.
- Mixing hot Piranha solution with organic compounds may cause an explosion. This includes acetone, photoresist, isopropyl alcohol (other organic solvents), and nylon.
- Containers used during the etching process 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 person responsible for the piranha etching process.
- Piranha Solution is very energetic and potentially explosive. It is very likely to become hot, more than 100°C. Handle with care. Picking up a beaker that is hot will be very painful, may melt your gloves, and may cause you to spill it.
- Do not transport solution around the room in beakers. Never pour chemicals back into the original container.
- Immersing a substrate into the solution should be done slowly to prevent thermal shock that may crack the substrate material.
- **AVOID INHALATION!** 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 CONTACT!** Don appropriate personal protective equipment (PPE):
 - Lab coat, full-length pants and closed toed shoes
 - Safety glasses or goggles
 - Acid-resistant apron, gloves with extended cuffs, and face shield required when handling large quantities outside of the fume hood (>500mL) or where splashing is more likely.
 - ALWAYS work behind the fume hood sash, wear a face shield when working with fume hood sash open higher than 16 inches from the base.
 - Consult the [EH&S Glove Selection Guide](#) to help choose the appropriate glove material that are rated for use with the specific concentration of Sulfuric acid, Hydrogen peroxide and Ammonium hydroxide (if applicable). Not all gloves are rated for use with both materials. Consult your Laboratory Safety Advisor for appropriate glove material.
 - Recommended Glove Material: Rubber, Butyl, Neoprene, or Viton (regular Nitrile gloves will not provide appropriate protection).
 - Recommended Gloves: Ansell Microflex 93-260 (Nitrile & Neoprene composite), Ansell AlphaTec® Solvex® 37-175 (Nitrile), Ansell AlphaTec® 38-514 (Butyl Polymer).

After Completing Work:

- Do not add any acids or bases to the solution once completed.
- Do not mix with organic waste compounds (e.g., acetone, methanol, isopropanol).
- 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.
- Leave the hot Piranha solution in an open container in a fume hood or ventilated enclosure until cooled.
- Dispose Piranha Solution waste following University Hazardous Waste Procedures.
 - Allow hot piranha solution to cool down, put the waste solution in a cleaned and dried container with a vented cap. You may request vented caps from the [Chemical Waste Pickup / Services Online Request](#). If 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. Hazardous Waste Classification: Oxidizer, Corrosive, and Toxic.

- Place the appropriately closed and labeled waste container into secondary containment, segregated from organic chemical waste. Place a label on the container declaring no other chemical waste streams should be added.

EMERGENCY PROCEDURES

First Aid:

SKIN CONTACT

- Solution may cause skin burns. Remove contaminated clothing. Flush the affected area with copious amounts of water for at least 15 minutes.
- Seek medical attention by calling 911.

EYE CONTACT

- Solution is corrosive and irritating to eyes.
- Flush contaminated eye(s) immediately with copious amounts of water for at least 15 minutes.
- Seek medical attention immediately by calling 911.

INHALATION

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

Spill Response:

- In case of an incidental spill, use the acid neutralizing agent (or alkaline neutralizer if base solution) in your spill kit. Do not use combustible organic materials (spill pads or paper towels) to clean up the spill unless it has been properly neutralized, and pH tested to a safe range of pH=6-8.
- If in doubt or a large spill occurs, contact University Operations Center at (617)495-5560 or HMS/HSDM Operations Center (617)432-1901 and request EH&S assistance.
- **OUTSIDE FUME HOOD OR VENTILATED ENCLOSURE:**
 - Alert others and evacuate to a safe distance and prevent entry.
 - Contact University Operations Center at (617)495-5560 or HMS/HSDM Operations Center (617)432-1901 and request EH&S assistance.
 - Restrict access to spilled area from lab personnel and post signage indicating hazardous spill of corrosive and potentially explosive piranha solution in the entrance to the lab.
 - Remain in a safe location until EH&S arrives.
- **INSIDE FUME HOOD OR VENTILATED ENCLOSURE:**
 - If trained and confident, don PPE described above and apply acid neutralizer then pH test to a safe range (pH=6-8). Collect spill material and dispose as hazardous waste following the hazardous waste disposal guidelines listed above.
 - If not confident or spill is too large to handle, contact University Operations Center at (617)495-5560 or HMS/HSDM Operations Center (617)432-1901 and request EH&S assistance.

SOURCES

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