Piranha Solution

Standard Operating Procedure

Revision Date: 11/20/2023

Laboratory Director (LD) Approval is Required Prior to Performing this Procedure

This standard operating procedure (SOP) outlines the preparation, disposal, handling, and use of piranha solution. Review this document and supply the information required in order to make it specific to your laboratory. In accordance with this document, laboratories should use appropriate controls, personal protective equipment, and disposal techniques when handling piranha solution.

All laboratory workers must read and understand the [Laboratory Emergencies SOP](https://ehs.umich.edu/wp-content/uploads/2022/05/LaboratoryEmergencyProceduresSOP.docx) prior to commencing any work in a laboratory.

# Description [Provide additional information as it pertains to your research protocol]

Piranha solution refers to a hot solution consisting of concentrated sulfuric acid and hydrogen peroxide, typically 3 parts sulfuric acid to 1 part 30% hydrogen peroxide. Piranha solution is highly corrosive and a powerful oxidizer capable of rapidly oxidizing organics and removes metals by forming complexes that stay in the solution. The solution can also make many surfaces hydrophilic by means of hydroxylation.

Common applications include removal organic residues, metal oxides and carbonates, and even elemental carbon usually resistant to dissolution. It is used in the preparation of glass and silicon substrates for cleaning of glassware, nanosphere lithography, in preparing surfaces for self-assembly, and in the detoxification of industrial wastewater.

The characteristics of piranha solution that make it an effective and useful laboratory product inherently pose significant hazards to its users. Given the name “piranha” for the solution’s nature to aggressively attack organic material, including human flesh. Use of piranha solution demands respect and consideration of the potential hazards.

A less hazardous, more stable solution such as AlNoChromix (formerly NoChromix) or Nanostrip should be used if possible. For certain applications, ionized oxygen plasma has been found to work just as well as, if not better, than Piranha.

## Process [Write the steps for using the chemical in your research protocol]

# Potential Hazards [Provide additional information as it pertains to your research protocol]

Physical hazards:

* Preparation of the solution is extremely exothermic. Even with gradual addition of hydrogen peroxide, this reaction can heat to over 100°C. Temperatures in excess of the boiling point can cause bubbling, frothing, and release of corrosive vapors.
* Piranha solution reacts rapidly with metal ions. Metal contamination during solution preparation can cause even 30% hydrogen peroxide to react vigorously raising the temperature to dangerous levels and release hydrogen gas. Explosion potential exists when hydrogen, oxygen, and heat are generated by the reaction. Metal tools and utensils should not be used in contact with piranha solution.

Corrosion hazards:

* Piranha is highly corrosive and its acidic vapors cause a severe inhalation hazard which can be destructive to the mucosal membranes and result in severe burns.
* Skin or eye exposure to piranha solution can cause severe burns.
* Piranha is incompatible with organic materials (including acetone, isopropyl alcohol, nylon, etc.), and can cause organic materials to spontaneously ignite.
* In the context of work in a fume hood, corrosion could break the cord sash, causing the sash to fall and cause severe injury to workers or damage the exhaust fan of the fume hood, exposing workers to dangerous exhaust emissions.

Fire and explosion hazards:

* An explosion or sudden release can result from storing piranha in a closed container due to pressure buildup. Never store piranha for later use, especially in a closed container.
* It will react with most metals and release flammable hydrogen gas (remember it is also an oxidizer), as well as provide enough heat for ignition if not handled properly.

Contact EHS for assistance in performing an exposure or hazard assessment.

# Engineering Controls [Provide additional information as it pertains to your research protocol]

* An eyewash and safety shower must be available in the immediate work area for any work with piranha.
* Always prepare and use piranha solutions inside a fume hood with the sash between you and the solution. This helps prevent inhalation hazards and provides some protection in case of an explosion or splashing.
* Label fume hoods with signage such as “Caution, Piranha Solution in Fume Hood, Highly Energetic and Corrosive”.

# Work Practice Controls [Provide additional information as it pertains to your research protocol]

* Piranha should only be used during normal working hours; never use or handle when working alone in the laboratory. Work within sight or hearing of at least one other person who is familiar with the hazards and procedures.
* Designate areas where piranha solutions are used. The work area should be cleared of all items not used in working with Piranha solution; in particular, no wash bottles should be stored in the same area.
* No chemicals, especially no poisonous or toxic chemicals, should be stored below the fume hood because, in the case of a spill, they may release dangerous gases.
* Only prepare enough solution for immediate use. Due to its extreme reactivity it has a relatively short usage life.
* Only make and use piranha in glass or Pyrex containers (the solution is incompatible with plastic). Use tools that are dedicated for Piranha work:
	+ an open-topped vessel for mixing Piranha, a beaker or dish to allow for any gas to easily escape (never a conical flask or bottle);
	+ a stirring rod to mix the sulfuric acid and hydrogen peroxide;
	+ Teflon tweezers to deposit and retrieve samples;
	+ a dedicated bottle with a vented cap to store neutralized Piranha waste and only neutralized Piranha waste, which should be placed in a secondary container;
	+ a funnel to help pour the waste into the waste bottle.
* It is recommended that you add hydrogen peroxide to sulfuric acid very slowly (adding the smaller amount to the larger amount). If the hydrogen peroxide concentration exceeds 50% an explosion could occur; adding the hydrogen peroxide to the acid avoids this situation. Mixing this solution should be done with extreme caution.
* If the mixture foams or smokes during the mixing procedure or afterward, it can indicate contamination by organics or other source. All work should be suspended until the solution has stabilized.

# Personal Protective Equipment [Provide additional information as it pertains to your research protocol]

* Wear closed-toe shoes (non-mesh upper), lab coat, safety goggles, face shield, acid apron, and chemical-resistant gloves when working with piranha.
* Sulfuric acid penetrates standard nitrile laboratory gloves in 5 minutes or less. Heavy rubber gloves are recommended when working with piranha.
* No exposed jewelry should be worn including necklaces, rings, metallic bracelets, or hair bands.
* There should be no exposed skin.

# Transportation and Storage [Provide additional information as it pertains to your research protocol]

Piranha should be made at its point of use and not transported or stored. Only make enough solution for immediate use. Piranha solution must be made fresh for each application and cannot be kept beyond its immediate application.

**Reaction between the solution components actively produces gas until the solution is stabilized and cannot be stored in a sealed vessel. Never** tightly seal piranha solution unless the solution has fully stabilized and reached room temperature. Specialized gas permeable caps are necessary for waste containers.

Allow waste or excess solution cool sufficiently inside the fume hood. When storing spent piranha etches for waste pickup, these containers should always be placed in secondary containment that is acid resistant. See the next section for detailed waste handling procedures.

# Waste Disposal [Provide additional information as it pertains to your research protocol]

After use, allow solution to cool in a labeled container inside a fume hood. Waste piranha etches should only be kept in glass containers; do not use plastic or metal containers. The container requires a piranha waste cap which allows the solution to vent and avoid bottle pressurization.

Waste containers and venting caps are available from Environment, Health & Safety (EHS) Hazardous Materials Management (HMM) [via their online request form](https://ehs.umich.edu/haz-waste/request-collection-and-supplies/) or by calling (734) 763-4568. When requesting supplies from EHS HMM, specify that piranha waste caps are needed. These caps fit the standard glass bottles supplied by EHS HMM. While waiting for pickup, piranha waste must be stored in the described container.

Do not add any other materials to piranha waste. **Label the waste container “For Piranha Solution Disposal ONLY – Do Not Add Other Types of Chemicals**.”

Waste solution must be cooled overnight or to room temperature prior to waste storage/disposal. Keep the solution in the fume hood until sufficiently cooled.

# Spill Procedure [Provide additional information as it pertains to your research protocol]

If any employee is in need of emergency medical attention, call 911 immediately.

* When a spill occurs, personal safety should always come first.
* Alert and clear everyone in the immediate area where the spill occurred.
* Attend to injured or contaminated persons and remove them from exposure.
* Use proper personal protective equipment as indicated above.
* Collect residue, place in container and contact EHS-HMM (734) 763-4568 for proper disposal.

If less than 200 ml of spent solution (no longer evolving gases) is spilled in the fume hood, lab personnel can soak up spill with absorbent/neutralizer for acid spills. Dispose of absorbent material as solid hazardous waste. Wipe contaminated area again with soap and water solution.

If reactive solution (still evolving gases) is spilled in the fume hood, or piranha solution is spilled OUTSIDE of the fume hood:

* Do not take any action to cover the spill.
* Alert people in the laboratory to evacuate.
* **Call University of Michigan Division of Public Safety and Security (DPSS) at 911 immediately for assistance.**
* Close doors to affected area.
* Post warnings to keep people from entering the area.
* Have person available that has knowledge of incident and laboratory to assist emergency personnel.

For additional information regarding spill response procedures, refer to the EHS [Hazardous Waste Spill Response](http://ehs.umich.edu/hazardous-waste/spill-response/) Web page.

# Training of Personnel

All personnel shall read and fully adhere to this SOP when handling piranha solution.

# Certification

I have read and understand the above SOP. I have received approval from my Lab Director to perform this procedure. I agree to contact my Lab Director if I plan to modify this procedure.

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### Major Revisions (Tracking purposes only -- Do not print as part of SOP)

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| Date | Revision |
| 09-19-18 | Updated EHS name and logo and format and revised the Exposure/unintended contact section (AKJ) |
| 02-25-19 | Updated links, certification and formatting (DML). |
| 05-25-22 | Updated the Description, Potential Hazards, Work Practice Controls, Transportation/Storage and Spill Procedures sections. (LGS) |
| 11-20-23 | General Revisions, Updated Waste disposal procedures (JMW) |

**References**

Schmidt, Hugo Gerald. (December 2021) *Safe Piranhas: A Review of Methods and Protocols*. ACS Chemical Health & Safety. DOI: 10.1021/acs.chas.1c00094. pp 54-61