**University of Arizona**

**Piranha Standard Operating Procedure**

*[This is a template. Fill in all necessary blanks and delete all highlighted areas when complete. Add any sections necessary for your laboratory. This will be appended to your Laboratory Chemical Hygiene Plan.]*

**Title:**  **Click here to enter the title of your SOP.**

**Approval Holder (AH):** Click here to enter text **Approval #:** Click here to enter text

**Approval Holder Phone Number(s):** Click here to enter text

**Approval Safety Coordinator (ASC):** Click here to enter text

**Approval Safety Coordinator Phone Number(s):** Click here to enter text

**Department:** Click here to enter text

1. **Purpose**

This standard operating procedure (SOP) is intended to provide guidance on how to safely use, storage, and disposal of piranha in Enter AH’s name’s laboratory. Laboratory personnel should review this SOP, as well as the appropriate Safety Data Sheet(s) (SDSs), before Describe the procedure or process this SOP will address. If you have questions concerning the requirements within this SOP, contact your Approval Holder (AH) or Approval Safety Coordinator (ASC).

1. **Scope**

*[Describe when this SOP applies and to whom this SOP applies.]*

1. **Hazard Description**

*[Describe the hazards presented by the procedure or process this SOP addresses. What makes it hazardous? Provide an example, if applicable.]*

 

Piranha solutions are a mixture of concentrated sulfuric acid with hydrogen peroxide, usually in a ratio of 3:1 to 7:1. They are used to remove trace amounts of organic residues, such as photoresist, from substrates. The mixing procedure is an exothermic reaction that can reach temperatures of 100⁰C or higher. The reaction of hydrogen peroxide on concentrated sulfuric acid produces highly activated and oxidizing peroxymonosulfuric acid (H2SO5), also called Caro’s acid [1].

Depending on the preparation procedure, piranha solutions can contain up to 5% peroxymonosulfuric acid. This highly reactive species makes piranha an efficient solution for oxidizing organics. Like most peroxides, peroxymonosulfuric acid can be highly unstable and/or explosive depending on conditions. Because piranha solutions are highly corrosive and oxidizing mixtures of sulfuric acid, peroxymonosulfuric, and hydrogen peroxide, they react violently with organic material and can cause an explosion. In addition, gas evolution can lead to pressure build-up and explosion if the solution is stored in a closed container.

Due to the described safety hazards and problems with safe disposal of waste solutions, **piranha should be used only if there is no other alternative**. Check if a less hazardous substitute such as KOH/ethanol, NoChromix, or Nano-strip can be used. Commercially available piranha etch solutions such as Nano-strip contain 10% peroxymonosulfuric acid and less than 1% hydrogen peroxide. These solutions are made from high purity compounds and provide a more stable, safer, and more consistent alternative to self-prepared piranha of varying quality.

1. **Process & Hazard Controls**

*[Describe the steps needed to set up and complete the procedure or process in safe manner following the* [*hierarchy of controls*](https://www.cdc.gov/niosh/topics/hierarchy/default.html)*. Use as much detail as is necessary to ensure all laboratory workers can complete the procedure or experiment safely.]*

* 1. **Elimination/Substitution**

*[Describe any eliminations of hazardous chemicals or processes; alternatively, any substitutions with less hazardous alternatives that could be used to accomplish the task. Delete this section if you are unable to eliminate or substitute.]*

* 1. **Engineering Controls**

*[Describe any engineering controls (e.g. fume hoods, gas cabinets, local exhausts, blast shields, etc.) that are used to safely accomplish the task.]*

Handling of piranha solutions must be done in a properly functioning fume hood compatible for acid use. Before you begin, lower the sash as much as possible to provide a barrier. The sash should be raised no higher than 18 inches to properly capture vapors and protect workers from potential splashes.

* Never remove an open container containing piranha from the hood.
* Clearly label the hood with a warning sign when there is piranha present (please visit the RLSS User Dashboard for GHS-compliant labels).
* Do not store any organic material in the hood while piranha solutions are present.
* Avoid heating piranha; if the solution has to be heated, wait until it has stabilized, then use a hotplate with over-temperature protection to prevent boil-over and do NOT leave it unattended.
* Avoid heating piranha solutions over long periods of time (more than one hour) as it only accelerates the decomposition of the active species leading to a less effective cleaning solution.
	1. **Work Practices**

*[Describe any work practices (e.g. staggering schedules, additional cleaning measures for particulates, etc.) that are used to safely accomplish the task.]*

**NEVER add any organics to piranha solution**, it could cause an explosion. Any chemical containing a C-H bond, e.g., acetone, isopropanol, ethanol, photoresist, detergents, is organic. Even small amounts of organics could make the piranha solution unstable.

* **Preparing Piranha solution**
	+ Prepare only as much Piranha as is immediately needed; do NOT create solutions in bulk quantities and store for future use.
	+ Prepare piranha solutions only in glassware or Teflon. Piranha reacts with many plastic materials. Make sure all glassware is clean and dry before using.
	+ Mix the hydrogen peroxide solution with the sulfuric acid SLOWLY and expect the container to become hot. The sudden increase in temperature may lead to boiling or even splashing.
	+ Any batch made over 100 mL requires cooling in an ice bath when mixed.
* **Using Piranha solution**
	+ Maintain a log of all additions to piranha waste bottles including the user’s name, date, time, amount, concentration (3:1, 5:1, etc)
	+ Do not keep piranha waste on hand for extended periods of time. The LAST ADDITION to a piranha waste bottle should be no later than 3 months after the first addition
	+ Do not place caps on piranha waste bottles
	1. **Personal Protective Equipment**

*[Describe the personal protective equipment needed to adequately protect laboratory workers when performing the process or procedure addressed by this SOP. Ensure to specify any personal protective equipment beyond the minimum (i.e. safety glasses, lab coat, gloves, long pants and closed-toed shoes).]*

* **Hand and Arm Protection:**
	+ At minimum, wear disposable gloves compatible with sulfuric acid; it is recommended that these are doubled to increase protection.
	+ Change gloves frequently and immediately after exposure.
	+ When handling large amounts (>500mL) or when splashing is more likely, wear acid resistant gloves with extended cuffs made from rubber, butyl, neoprene, or viton.
	+ Always check the gloves for holes.
	+ Wash hands with soap and water after removing gloves.
* **Eye and Face Protection** Splash goggles are the minimum eye protection. A face shield should also be worn.
* **Body Protection**: an acid resistant apron above a lab coat, or an acid smock should be worn whenever there is no barrier to prevent splashes to the face/body (e.g., when the sash is raised).
* **Respiratory Protection**: Respirators may be required if exposures are not able to be adequately controlled by the use of engineering controls or other means. All uses of respiratory protection require RLSS assessment and consultation (for assessment of work, selection of respirator and filtration, and OSHA-mandated medical clearance and fit testing). Contact rlss-ppe@arizona.edu with any questions or concerns.
	1. **Transportation and Storage**

*[Describe how to safely transport and/or store (e.g. ventilated cabinet, flammable cabinet, under inert blanket, etc.) the hazardous chemical(s) or processes.]*

* **Storage**
	+ Store sulfuric acid in an acid cabinet. Hydrogen peroxide solutions should be stored in a refrigerator to slow decomposition. Refer to section 7 of the SDS for storage instructions.
	+ Due to its highly reactive nature, do not store piranha solution. Mix it fresh for each application.
1. **Spills, Cleanup & Disposal**

*[Describe how to safely end the procedure or process, clean up the process or spills, and/or dispose of any waste generated.]*

**Spills**

Spill response should always follow the [University Chemical Hygiene Plan](https://rgw.arizona.edu/sites/default/files/cs-univeristy_chemical_hygiene_plan.pdf) Section 8.2. Please find general guidance below:

* Do NOT use paper towels, rags, or other organic material to absorb a spill as they may spontaneously ignite

**Exposure Response**

|  |  |  |  |
| --- | --- | --- | --- |
| **Inhalation** | **Ingestion** | **Skin Contact** | **Eye Contact** |
| May irritate the respiratory tract.  Conscious persons should be assisted to an area with fresh, uncontaminated air.  Seek medical attention in the event of respiratory irritation, cough, or tightness in the chest.  Symptoms may be delayed. | Rinse mouth. Do not induce vomiting. Seek medical attention immediately. | May cause skin burns.  Flush the skin with copious amounts of water for at least 15 minutes.  Seek medical attention immediately. | Corrosive and irritating to the eyes.  Flush contaminated eye(s) immediately with copious quantities of water for at least 15 minutes.  Seek medical attention immediately. |

* **Disposal**
	+ If possible, neutralize spent piranha solution as you generate it. Put five times as much ice as the amount of the solution you want to neutralize into a container large enough to hold the ice, the piranha and the neutralizing solution (e.g., use 500 g of ice for 100 ml piranha solution). Pour the spent piranha solution onto the ice and then slowly add 1M sodium or potassium hydroxide solution while stirring until a neutral pH is reached.
	+ Alternatively, if no ice is available, fill the bottom of a container (10 times the volume of the piranha solution) 1 inch high with dry sodium bicarbonate and cover it with water. Slowly pour the piranha solution in small portions onto the sodium bicarbonate. Carbon dioxide will form, and the solution can quickly foam over. Stir and wait for the gas to escape before adding more piranha solution. Make sure that solid sodium bicarbonate is left at the bottom of the container and add more if it is used up.
	+ If the waste solution does not contain any regulated metals (arsenic, barium, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, zinc), the neutralized solution can be poured down the drain.
	+ Used piranha cleaning solution is still concentrated sulfuric acid with an undetermined hydrogen peroxide concentration. Care must be taken not to allow the solution to be mixed with organic solvents, as this will cause a violent reaction and possibly an explosion.
	+ Do not place caps on piranha waste bottles.
1. **Enter Additional Section Title**

*[Add as many sections as necessary to adequately describe how to safely perform the procedure or process addressed by this SOP.]*

1. **References**

University of Illinois SOP:

<https://drs.illinois.edu/Page/SafetyLibrary/PiranhaSolutions>