

**Standard Operating Procedure for Using Piranha Solution**

Print a copy and keep with your Safety Data Sheets and training documents.

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| Department |  |
| Principal Investigator (PI) |  |
| PI Phone Number |  |
| Lab Manager |  |
| Lab Manager Phone Number |  |
| Emergency Contact |  |
| Emergency Contact Phone Number |  |

1. **Purpose**

The purpose of this document is to provide the information necessary to safely use piranha solution in the \_\_\_\_\_\_\_\_\_\_\_ laboratory and to comply with requirements of the UNM Piranha Solution Safety Program and the OSHA standard 29 CFR 1910 Subpart Z.

1. **Hazard Identification:**

***Strong oxidizer* --**

Piranha solution, also known as piranha etch, is a mixture of sulfuric acid (H2SO4) and hydrogen peroxide (H2O2), used to clean organic residues off substrates. Because the mixture is a strong oxidizer, it will remove most organic matter, and it will also hydroxylate most surfaces (add OH groups), making them extremely hydrophilic (water compatible). Piranha solution is used frequently in the microelectronics industry, e.g. to clean photoresist residue from silicon wafers.

Piranha solution is very dangerous, being both strongly acidic and a strong oxidizer.Before using Piranha, a worker should attempt more stable methods of removing stains, tars or clogs. Often, glassware will "clean itself" if simply left with a rinse of a cleaning solution present. An immediate example for a suitable substitute, prior to using Piranha, is 98% sulfuric acid.

***Explosion hazard –***

Mixing of the solution ingredients is exothermic. The resultant heat can bring solution temperatures up to 120°C. One must allow the solution to cool reasonably before applying any heat. The sudden increase in temperature can also lead to violent boiling, or even splashing of the extremely acidic solution. Also, explosions may occur if the peroxide solution concentration is more than 50%. A 30% peroxide in water solution is more reasonable.

Many different mixture ratios are commonly used, and all are called piranha. A typical mixture is 3:1 concentrated sulfuric acid to 30% hydrogen peroxide solution; other protocols may use a 4:1 or even 7:1 mixture. A closely related mixture, sometimes called "base piranha", is a 3:1 mixture of ammonium hydroxide (NH4OH) with hydrogen peroxide. Base piranha is also known under the name of TL1 cleaning.

The traditional piranha solution is a 3:1 mixture of sulfuric acid and 30% hydrogen peroxide. The solution may be mixed before application or directly applied to the material, applying the sulfuric acid first, followed by the peroxide. Piranha solutions are extremely energetic and may result in explosion or skin burns if not handled with extreme caution.

1. **Engineering & Administrative Controls**

Piranha solution must only be handled/used within the chemical fume hood, which is designed to pull air and fumes up and away from the user (Engineering Control).

All lab personnel who use piranha solution must be trained on the hazards of piranha solution, including being familiar with this SOP (Administrative Control).

The door to the \_\_\_\_\_\_\_\_\_\_ lab is posted with signage indicating the presence and hazards associated with piranha solution (Administrative Control).

1. **Personal Protective Equipment (PPE)**

* *Hand Protection*: At a minimum complete protection of the skin is essential. Neoprene or nitrile gloves are recommended.
* *Eye Protection*: Safety glasses or splash goggles must be worn when handling piranha solution. A face shield is recommended.
* *Skin and Body Protection*: A lab coat must be worn when handling piranha solution.
* *Respiratory Protection*: Piranha solution should always be used in fume hood

1. **Standard Operating Procedures for Handling Piranha Solution:**

Handling

* 1. DO not breathe vapor. Always use glass (preferably Pyrex) containers. Piranha will melt plastics.
  2. Mix the solution in a fume hood with the sash between you and the solution. Wear gloves and eye protection.
  3. When preparing the piranha solution, always add the peroxide to the acid.
  4. Piranha solution is very energetic and potentially explosive. It is very likely to become hot, more than 100 degrees C. Handle with care.
  5. Leave the hot piranha solution in an open container until cool.
  6. Never store piranha solutions for longer periods. **Piranha stored in a closed container will likely explode.**
  7. Adding any acids or bases to piranha or spraying it with water will accelerate the reaction. This also includes Photoresist, which is a strong base.
  8. Mixing hot piranha with organic compounds may cause an explosion. This includes acetone, photoresist, isopropyl alcohol (other organic solvents), and nylon.
  9. Piranha solution that is no longer being used should never be left unattended if hot. Dispose of unneeded solution as soon as possible. **Do not store in a closed container.**
  10. Adding anything to the piranha solution (such as a substrate that may have organic residue), must be done slowly and carefully, giving the solution time to stabilize.
  11. Once the mixture has stabilized, it can be further heated to sustain its reactivity. The hot (often bubbling) solution will clean organic compounds off substrates, and oxidize/hydroxylate most metal surfaces. Cleaning usually requires about 10 to 40 minutes, after which time the substrates can be removed from the solution.
  12. The solution may be mixed before application or directly applied to the material, applying the sulfuric acid first, followed by the peroxide.
  13. Due to the self-decomposition of hydrogen peroxide, piranha solution should be used freshly-prepared. Any leftover Piranha solution should be properly disposed of as soon as possible.
  14. Immersing a substrate (such as a wafer) into the solution should be done slowly to prevent thermal shock that may crack the substrate material.
  15. It is important to remember that the solution, whilst susceptible to aging, will remain a significant hazard as it drips off the item being cleaned.
  16. Do not store piranha solution. Prepare it fresh as needed, and dispose of as hazardous waste when operation is complete.
  17. As they deem necessary, the PI/supervisor should insert here any information about whether a special use-area is designated for this material/process.
  18. Add appropriate lab-specific information here describing how this material(s) is generally used. E.g., name of protocol, typical frequency done, quantities used, temperature and any additional safety measures, etc.

NOTE: Vented caps will not vent quickly enough to avoid an explosion when dealing with fresh piranha solution, or piranha solution that is currently reacting with organic residue. **Containers with vented caps should be considered closed containers and therefore avoided as noted above. Only cap piranha waste containers with these vented caps, and then only immediately before waste pickup. Waste pickup should be requested only after the piranha solution has** cooled **and decomposition has stopped.**

1. **Chemical Disposal**

Use glass (preferably Pyrex) containers to store waste. Do not mix with other hazardous waste streams. Schedule waste pickup immediately after completion of operation requiring piranha solution. Keep container un-capped or loosely capped until immediately before waste pickup. **Waste pickup should be requested only after the piranha solution has cooled and decomposition has stopped.**

All chemical waste must be disposed of in accordance with Federal and State regulations and UNM's Chemical Hygiene Plan. Piranha solution and piranha solution-containing wastes should be collected in suitable containers and properly labeled as soon as waste is added to the containers. Piranha solution waste should be labeled as such:

**HAZARDOUS WASTE**

**Piranha Solution Waste**

**Toxic, Corrosive, Reactive**

Call EHS at 277-2753 to schedule a pickup of waste piranha solution and/or other waste chemicals.

1. **Spill Procedures:**

For small/minor spills (<1L), use the materials in the spill kit to clean up the spill. Minimum PPE for cleaning up a piranha solution spill is safety glasses/goggles, gloves and lab coat. The spill clean-up materials must be double-bagged, tightly closed, labeled and picked up by EH&S for disposal.

Spills in excess of 1L of piranha solution should not be cleaned up by lab personnel. In the event of a large/major spill of piranha solution, evacuate the area and call:

* Campus Police -- 911 on a landline or 505-277-2241 on a mobile phone, and
* Environmental Health & Safety (EH&S) – 505-277-2753 during business hours, or
* EH&S Duty Officer Pager -- 505-951-0194 (enter your phone number after the message)

1. **First Aid Procedures**

In the event of a Piranha solution exposure, seek immediate medical attention.

* Skin Contact and Eye Contact should be washed immediately in safety shower or eyewash respectively for 15 minutes.
* If the exposure is severe, seek medical attention at the emergency room. If heading to UNMH, a non-injured person should contact the UNMH charge nurse in advance at 505-604-9349 with information on the chemical and nature of exposure.
* UNM employees should contact Employee Occupational Health Services (EOHS) at 505-272-8034.
* UNM students should contact Student Health Services at 505-277-7810.
* If the exposure occurs after hours, employees and students should seek medical treatment at a hospital emergency room.
* The supervisor of the injured person and EH&S must be notified as soon as possible after the exposure.
* The notice of Accident, Incident, or Spill form should be filled out on the EH&S website.

1. **Other Emergencies**

**Fire or Medical Emergency -- Dial 911**

**Life-Threatening Emergency, After Hours, Weekends and Holidays** – **Dial 911**

**Non-Life Threatening Emergency** – Call EH&S at 505-277-2753 to seek assistance and report the incident.

**Training Requirements**

All lab personnel who use piranha solution must review the lab specific Piranha Solution SOP before beginning work.

**Principal Investigator SOP Approval**

By signing and dating here, the Principal Investigator certifies that this Standard Operating Procedure (SOP) for Using Piranha Solution is accurate and provides information sufficient to safely use piranha solution in the \_\_\_\_\_\_\_\_ laboratory.

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Signature Printed Name/Title Date

I have read and understand the content of this SOP:

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| **Name** | **Signature** | **Date** |
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