



## Standard operating procedure for hazardous chemicals

### **Piranha solution**

The content of this document was edited by Raluca Gearba

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### Risk Assessment

**Hazardous Chemicals:** *(List chemicals used. Include chemical name, common name and abbreviation)*

Acidic Piranha etch (or Piranha) is a mixture of varying ratios of concentrated sulfuric acid (typically 98% concentration) and hydrogen peroxide (usually 30% concentration) used to clean organic residues from substrates.

Never use hydrogen peroxide in higher concentrations.

- 1) *Sulfuric acid, CAS #7664-93-1*
- 2) *Hydrogen peroxide, CAS #7722-84-1*

**Potential Hazard(s):** *(Describe the potential hazards associated with the chemicals or the procedure.)*

*Piranha is highly energetic and has many potential hazards. A less hazardous solution/process should be used if possible.*

- 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.
- Piranha is incompatible with organic materials (including acetone, isopropyl alcohol, nylon, etc), acids, and bases.  
Piranha is a very powerful oxidizer and can cause organic materials to spontaneously ignite.
- 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.

- When the solution is made (or comes in contact with organic materials) the reaction is exothermic. This reaction can heat to over 100°C.
- 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.

**Routes of Exposure:** *(As applicable, describe the potential routes of exposure associated with the procedure such as inhalation, injection, skin/eye contact)*

*Piranha solution is highly corrosive and a highly oxidizing agent.*

- Skin contact: Remove contaminated clothing, rinse affected area with water for at least 15 minutes. Seek medical attention.
- Eye contact: Immediately flush eyes with water for 20 minutes while holding eyelids open. Seek medical attention. Place ice packs on the eyes while in transit to medical facility.
- Ingestion: Do not induce vomiting and seek medical attention immediately.
- Inhalation: Remove exposed individual to fresh air. Seek medical attention in the event of respiratory irritation, cough, or tightness in the chest. Symptoms may be delayed.

For minor injuries and exposures to hazardous materials during regular business hours call the HealthPoint Occupational Health Program: 512-471-4647.

**In the event of a fire, serious injury, or other life threatening situation, call 911.** Remember to have your name, number, location, and any other pertinent information available at the time of the call. It is important to inform the safety office and the police if anyone has been injured or if there has been a personal exposure.

Campus Police phone number: 512-471-4441

**Quantity/Concentration Hazards:** *(As applicable, describe if the quantity/concentration of the chemical increases the risk associated with exposure to the chemical.)*

Skin or eye exposure to Piranha solution can cause severe burns. Always limit the amount of Piranha solution.

- The OSHA Permissible Exposure Limit (PEL) and ACGIH Threshold Limit Value (TLV) for sulfuric acid are both 1 mg/m<sup>3</sup> as an 8-hour time-weighted average.
- The OSHA PEL and ACGIH TLV for hydrogen peroxide are both 1 ppm as an 8-hour time-weighted average

**Substitution of Less Hazardous Chemicals:** *(As applicable, describe the potential use of less hazardous chemical substitutes)*

*Piranha solutions should only be prepared and used when necessary. Try to avoid using it if a less reactive agent works. Piranha solution is not recommended for routine cleaning of glassware.*

*Contact EHS lab safety staff at 512-471-3511 for a possible alternative.*

Alternative route for surface cleaning: 5 minutes successive sonication in acetone, methanol and isopropanol is an effective alternative method for removal of organic residues from surfaces.

### **Control Measures**

**Personal Protective Equipment (PPE):** *(List all applicable personal protective equipment needed for procedure)*

- 1) Wear closed-toed shoes (non-mesh upper), safety glasses, full face shield, acid apron, and chemical-resistant gloves when working with Piranha.
- 2) Work in a clean, properly working hood with the sash down
- 3) Sulfuric acid penetrates standard nitrile laboratory gloves in 5 minutes or less. Heavy rubber gloves are recommended when working with Piranha.
- 4) No exposed jewelry should be worn including necklaces, rings, metallic bracelets, or hair bands.

**Engineering Controls:** *(As applicable, describe the engineering controls used for the procedure)*

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.

**Work Practice Controls:** *(As applicable, describe work practice controls used for the procedure)*

- Only make and use Piranha in glass or Pyrex containers (the solution is incompatible with plastic).
- Only prepare enough solution for immediate use. Due to its extreme reactivity it has a relatively short usage life.
- **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.
- Do not mix Piranha with incompatible materials including acids, bases, and organic solvents (acetone, isopropyl alcohol, etc). Do not store bottles/materials containing organic compounds or other incompatibles in the fume hood with Piranha.
- Handle the container with care as it may be hot from the exothermic reaction.
- Ensure all substrates are rinsed and dried before Piranha solution comes in contact with them.
- Never put Piranha in an airtight container.
- Always keep acid neutralization materials at all locations where Piranha is made or used in the lab.
- Do not use or store metal tools or accessories that will directly contact Piranha solution.

- Work within sight and/or hearing of at least one other person who is familiar with the hazards and written procedures.

Once work with Piranha is complete, wipe down the area with a soap and water solution.

**Monitoring:** *(As applicable, describe any monitoring needed for the procedure)*

*Non applicable*

**Use in Animals:** *(As applicable, describe how the chemical will be safely used in animals)*

*Non Applicable*

**Cleanup Procedures:** *(Describe the process for cleaning the work area during and after the procedure.)*

Before starting the procedure the user needs to ensure that all surface are clean and dried and no organic solvents are present in the hood.

At the end of the procedure all beakers need to be cleaned with water and soap and dried.

The waste solution should be disposed of in accordance with the procedure described below.

**Storage Procedures:** *(Describe how and where the chemical will be safely stored)*

Hydrogen peroxide should be provided by the user and removed from the cleanroom after each use. Sulfuric acid is provided by TMI and is stored in a secondary containment under the acids hood. Due to its highly reactive nature, Piranha should not be normally stored. Mix fresh solution for each use. After use dispose of the solution as described in the waste disposal procedure below.

**Transportation Procedures:** *(If the chemical will be transported on campus, describe procedure)*

Piranha solutions should not be stored. Only make enough solution for immediate use. Never cap Piranha waste unless it has cooled overnight or to room temperature (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

The waste container should have a waste tag attached. Do not mix Piranha waste with any other waste. The waste container should be for Piranha use only.

The waste tag should contain the name of the generator, phone number and location (filled in my TMI staff) as well as the contents (sulfuric acid, 75%, hydrogen peroxide (30 wt. %), 25%).

Never fill in the waste container more than 2/3.

**Waste Disposal Procedures:** *(Description of how waste will be disposed)*

At the very least- After use, allow solution to cool and stop reacting in a labeled, open container inside a fume hood. Waste solution must be cooled overnight or to room temperature, and the reaction must go to completion, prior to waste storage/disposal. **After you believe the reaction has stopped, swirl the bottle to ensure that no further bubbling takes place. Cap the container only after the waste solution has cooled completely and there are no more bubbles being formed.**

Do not add any other materials to Piranha waste.

Whenever possible neutralize the Piranha solution using the procedure below (only performed by TMI Staff):

1. Let the piranha solution to cool down to room temperature or overnight
2. Transfer the Piranha in the dedicated 4,000 ml beaker
3. Dilute the piranha with water at least 8 times
4. Add sodium carbonate slowly (Ex: for 40 ml piranha 3H<sub>2</sub>SO<sub>4</sub>:1H<sub>2</sub>O<sub>2</sub> add 120g sodium carbonate); The solution will start to bubble, wait for 10 min and then check the PH of the solution using PH paper; the neutralization is complete if the PH is 7 (orange or green color).
5. Wait until the neutralized solution cooled down before placing it into the waste container
6. At the end rinse the 4,000ml beaker with water

The TMI staff will arrange for the piranha waste to be picked up by EHS.

**Emergency Procedures:** *(Describe what procedures should be followed in the event of an emergency)*

**Spills or Releases:** *(Provide specific instructions on what personnel should do in the event of a spill or gas release. Include location of spill kits.)*

*Keep spill cleanup materials at locations where the solutions are prepared.*

*Notify the TMI staff and your supervisor*

*Small spills may be absorbed with wet paper towels. Keep towels wet and collect for chemical waste disposal. Contact EHS for spill assistance if needed*

*Large spills: immediately call 911 to report a piranha solution spill that is health threatening and contact EHS for spill assistance if needed. Contact CNM staff and your supervisor.*

**Fire:** *(Provide specific instructions on what personnel should do in the event of a fire)*

In case of a small fire and if properly trained use the fire extinguisher located to the right of the acids hood.

Inform the TMI Staff and your supervisor.

In case of an extensive fire call 911 immediately.

**Emergency Shut Offs:** *(If applicable, describe procedures for shutting down equipment in an emergency)*

In case there is a need to leave the area because of an emergency please leave the sign "Piranha solution in use" sign on the hood in clear view.

Leave the Piranha in an open container to cool down

Make sure no organic compounds are in the hood

**Signs and Symptoms of Exposure:** *(Describe the specific signs and symptoms of an exposure to the chemical)*

**Exposures:** *(Provide specific instructions on what personnel should do in the event of an exposure)*

*Piranha solutions are highly corrosive and a highly oxidizing agent.*

- Skin contact: Remove contaminated clothing, rinse affected area with water for at least 15 minutes. Seek medical attention.
- Eye contact: Immediately flush eyes with water for 20 minutes while holding eyelids open. Seek medical attention. Place ice packs on the eyes while in transit to medical facility.
- Ingestion: Do not induce vomiting and seek medical attention immediately.
- Inhalation: Remove exposed individual to fresh air. Seek medical attention in the event of respiratory irritation, cough, or tightness in the chest. Symptoms may be delayed.

**Occupational Health Requirements:** *(Describe any Occupational Health requirements necessary that are associated with the procedure. Examples include medical evaluation, baseline serum samples and respiratory fit testing)*

There is no specific evaluation required prior to the use of this specific procedure

**Material Safety Data Sheets (MSDS):** *(Describe how personnel will access MSDS in the lab. Include a copy of the MSDS with this SOP)*

The MSDS for sulfuric acid and hydrogen peroxide are attached to the present SOP as well as stored in a folder outside of the cleanroom in the viewing area.

**Training Requirements:** *(Describe what training personnel must complete before using chemical/procedure. This training should be documented)*

The users must complete the General Cleanroom training (NT 201 class which has as requirement the OH101 OH201 courses)

**Review of Procedure:** *(Describe the frequency for reviewing the SOP document)*

The present SOP will be reviewed every 6 months.

**Protocol:**

*Description of how to safely perform the experiment or operation.*

***DO NOT USE MORE THAN 100ML PIRANHA SOLUTION FOR ANY GIVEN RUN***

1. You need to reserve the Acids hood before use.
2. Before making the Piranha solution make sure that there is a waste container available (with a waste tag attached for Piranha use only) and estimate if the amount of waste you are about to generate can be still added. If not stop and contact the TMI staff.  
The waste container should be located under the hood (secondary containment provided as well)
3. Make sure that all surfaces are dry and clean.
4. Make sure that the saturated solution of sodium bicarbonate is available. If not make some. The sodium bicarbonate should be under the hood. Place some in the dedicated squirt bottle and add water.
5. Make sure that no organics are present in the hood.
6. Locate the spill kit.

7. Make sure that you have wet towels around in case of a small spill.
8. Be aware of where the eye wash and shower are located.
9. Make sure that other people are around and aware of the procedure.
10. Post the “Piranha solution in use” and “NO OTHER PROCESSES ALLOWED AT THIS TIME” sign on the hood in clear view.
11. Place the big Teflon tray labeled “Piranha Solution station” in the hood.
12. It is recommended to use Piranha solutions made of sulfuric acid and hydrogen peroxide (30%) in a 3:1 ratio. Do not use hydrogen peroxide more than wt. 30%.
13. Use the dedicated graded cylinder (they should be labeled) to measure the amount for each chemical
14. Locate the container to be used for the solution. It needs to be labeled: Piranha solution and add the acid.
15. Slowly add the peroxide; be aware that the reaction is exothermic.
16. Using a Teflon tweezer place the substrates to be cleaned into the Piranha solution and wait 10 15 minutes
17. NEVER LEAVE THE HOOD UNATTENDED WHILE PIRANHA SOLUTION IS STILL THERE. YOU CAN LEAVE THE HOOD ONLY AFTER THE WASTE HAS BEEN DISCARDED AND THE HOOD IS CLEAN.
18. Add 1,000 ml DI water to the two 2,000ml beakers labeled Water.
19. Retrieve the substrate from the Piranha solution and deep it in the first water beaker few times
20. Then do the same in the second water beaker.
21. At the end rinse the substrate thoroughly with DI water.
22. Dry the substrate with nitrogen.
23. Take the waste container and place it inside the Teflon tray. Remove the cap. Use the dedicated funnel to pour the Piranha solution in the waste container. MAKE SURE THE SOLUTION IS COOLED TO ROOM TEMPERATURE BEFORE PLACING THE CAP BACK. DO NOT FILL THE WASTE CONTAINER MORE THAN 2/3. Make sure you did not spill on the outside of the container. If yes, use large amount of water to clean it and/or the saturated solution of sodium bicarbonate.
24. Clean all the containers used (crystallizing dishes, Petri dishes, cylinders, funnel,... )with large amounts of water and dry them.
25. Clean the tray with water and soap as well if necessary.
26. At the end check all surfaces with Ph paper.
27. Remove the “Piranha solution in use” sign.
28. Report any problems encountered to Raluca Gearba at [gearba@austin.utexas.edu](mailto:gearba@austin.utexas.edu).
29. Non trained people can assist to the procedure only if they wear the appropriate PPE (apron, safety glasses, face shield and acid resistant gloves)





