
PIRANHA SOLUTION SAFETY GUIDELINES

The Piranha solution is used in etching processes to remove organic residues from substrates. Two different solutions can be used. The most common is the acid Piranha which consists of a 3:1 mixture of concentrated sulfuric acid (H_2SO_4) with 30% hydrogen peroxide (H_2O_2). Also used is the base Piranha which is a 3:1 mixture of ammonium hydroxide (NH_4OH) with 30% hydrogen peroxide (H_2O_2). 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. Anyone who works in laboratories containing Piranha solution should familiarize themselves with its SDS and a clear Standard Operating Procedure (SOP) should be established. Therefore, careful precaution should always be taken when handling this solution. This document discusses the properties, health and safety hazards, how to properly handle and store a Piranha solution. Also included are emergency procedures for dealing with accidental Piranha solution contact, including first aid treatment information.

⚠️*WARNING⚠️: Piranha solutions are VERY DANGEROUS! In addition to being a corrosive liquid and a strong oxidizer, there are many things which will cause the reaction to accelerate out of control ranging from foaming out of its bin to an explosion with a huge shock wave with possible acid (or base)-gown shredding glass sharps. Piranhas burn (oxidize) organic compounds. If you provide sufficient fuel for them (i.e., photoresist, IPA), they will generate enormous quantities of heat and gas. Always contact EHS when Piranha solutions are planned to be used: an SOP will be necessary

1. Properties

Names:

Chemical name: *Piranha solution, Piranha etch*

Solution: a) *Acid Piranha: usually mixture of 3:1 sulfuric acid and 30% hydrogen peroxide (but some protocols call for as much as 7:1 mixtures)*
b) *Base Piranha: usually mixture of 3:1 ammonium hydroxide and 30% hydrogen peroxide*

Chemical Formulas:

Sulfuric Acid: H_2SO_4

Ammonium Hydroxide: NH_4OH

Hydrogen Peroxide: H_2O_2

CAS #: Sulfuric Acid: 7664-93-9; Ammonium Hydroxide: 1336-21-6; Hydrogen Peroxide: 7722-84-1

2. Hazard Classification

Sulfuric Acid (concentrated)

WHMIS (2015):



Corrosive to metals (Category 1)
Skin Corrosion/irritation (Category 1A)
Serious Eye Damage/Eye Irritation (Category 1)
STOT (single exposure) Target Organs - Respiratory system (Category 3)

NFPA 704:



Flammability: Non-flammable
Health hazard: Highly toxic; severe acute and chronic health effects.
Instability/Reactivity: Sulfuric acid mixtures with certain compounds can be unstable and lead to explosion. Reacts violently with water.

Hydrogen Peroxide (20-40% w/w in water)

WHMIS (2015):



Oxidizing liquids (Category 2)
Corrosive to metals (Category 1)
Skin Corrosion/irritation (Category 1A)
Serious Eye Damage/Eye Irritation (Category 1)
Acute Oral Toxicity (Category 4)
Acute Inhalation Toxicity – Dusts & Mists (Category 4)

NFPA 704:



Flammability: Non-flammable
Health hazard: Hazardous in case of skin/ eye contact or ingestion.
Instability/Reactivity: Unstable at high temperatures. Slightly explosive in the presence of open sparks or flames, heat or organic materials, metals and acids.

Ammonium Hydroxide (25-30% w/w in water)

WHMIS (2015):



Skin Corrosion/irritation (Category 1B)
Serious Eye Damage/Eye Irritation (Category 1)
STOT (single exposure): Target Organs - Respiratory system. (Category 3)

NFPA 704:



Flammability: Non-flammable
Health hazard: Very hazardous in case of skin and eye contact or ingestion.
Instability/Reactivity: Stable however can form explosive compounds when mixed with heavy metals or halogens.

3. Reactivity, Fire and Explosion Hazards

The Piranha solution is very energetic, exothermic and potentially explosive. It is very likely to become hot, more than 100°C. Handle with care! When preparing the acidic version of the Piranha solution, always add the peroxide to the acid. The H₂O₂ is added immediately before the process because it immediately produces an exothermic reaction with gas (pressure) release. If the H₂O₂ concentration is at 50% or greater, **an explosion could occur**. Piranha solution reacts violently with any organic materials. Avoid mixing with incompatible materials such as acids, bases, organic solvents (acetone, isopropyl alcohol) or nylon. Always ensure that all substrates are rinsed and dried before placing them in a Piranha solution. Only use clean glass or Pyrex containers; Piranha solutions are not compatible with plastic.

4. Health Hazards

Piranha solution is a strong oxidizer. Both liquid and vapour forms are extremely corrosive to skin and respiratory tract. Direct contact will create skin burns and will be extremely destructive to mucous membranes, upper respiratory tract and eyes.

5. Safety Precautions for Piranha Solution Use

a) Training

Students and employees who handle Piranha solutions must have received training on the hazards of Piranha solutions from their respective department. They must know what to do in the event of a spill or an exposure incident. The SDS of the different components of the solution must always be kept within the immediate vicinity of the working area along with the Standard Operating Procedure (SOP) developed by the student / employee's department.

b) Ventilation / Fume Hood

Because highly corrosive vapors are generated when preparing Piranha solutions, all work should be conducted inside a certified chemical fume hood.

c) Eye Protection

Splash goggles and a face shield **MUST** be worn when handling Piranha solutions.

d) Gloves

Regular nitrile gloves do not provide sufficient protection. Heavy duty neoprene or rubber gloves must be worn.

e) Protective Clothing

The handling of Piranha solutions requires special protection equipment in addition to the standard laboratory clothing (lab coat). A corrosive-resistant Neoprene apron must be worn on top of the lab coat. Legs should also be covered by wearing a full size chemically resistant suit. Close leather shoes must also be worn.

f) Safe Work Practice

1. Always consider the use of less hazardous solutions or processes before using Piranha solution (e.g., safer cleaning solutions such as ultrasonic baths, Phosphate-based detergents, stabilized [Nano-Strip®](#) formulation, [Alnochromix](#) from Alconox, [Pierce RBS™-35 detergent](#), [PCC-54™ detergent concentrate](#)).
2. Piranha solution should be contained in glass or Pyrex containers. Piranha will melt plastics.
3. Always add hydrogen peroxide to sulfuric acid slowly. Never vice versa.
4. The hydrogen peroxide component should typically be kept to below 30%, never to exceed 50%.
5. Prepare small amounts to be used up for each application. Do not store Piranha solution in stock.
6. Adding any acids or bases to piranha or spraying it with water will accelerate the reaction.
7. Do not mix Piranha solution with incompatible materials (e.g., organic acids/bases/solvents).
8. Ensure containers are rinsed and dried before coming into contact with the Piranha solution.
9. Leave the hot Piranha solution in an open container until cool.
10. Do not seal containers containing Piranha solution. Avoid using airtight containers as pressure can build up inside of them.
11. Never use Piranha solution unless another, knowledgeable person is accompanying you, should an emergency situation occur.
12. Do not store wash bottles containing organic compounds on the Piranha deck.

6. Storage, Spill and Waste Issues

a) Storage and Waste Handling

Do not store Piranha solution. Mix fresh solution for each use. The primary hazard from storage of Piranha etch waste is the potential for gas generation and over pressurization of the container when the solution is still hot. If you store a hot solution in an air tight container, it will explode! Prior to discarding the Piranha solution, it must be left in an open container in order to cool down for several hours (overnight or over weekend) in a fume hood. **It is the researcher's responsibility to make sure that the open container is clearly labeled and left in a safe area for overnight cool down.** Once cooled down, the waste solution has to be stored in a waste container, ideally in an empty 4L glass bottle of sulfuric acid, equipped with a vented cap. EHS should be contacted for this specific type of cap.

Note the time and date of transfer(s) and also note if either heat or gas evolved after gentle swirling of the waste bottle.

A Piranha waste bottle can be considered cleared for disposal after the second consecutive agitation with a minimum separation of 48 hours with no reaction observed.

Few recommendations:

- ✓ **The vented cap must be maintained! It will be replaced by the original cap at the time of the waste pick-up and returned to the user for future experiments.**
- ✓ **Do not over-fill Piranha waste bottles: Leave at least 2" of head space in each bottle.**
- ✓ **Never use a plastic bottle as a Piranha solution waste container!**
- ✓ **Contact EHS (hazardouswaste@concordia.ca) for the waste pick-up that will be performed for the Piranha solution glass container at least 3 days after having been considered cleared for disposal.**

Additionally, some procedures need to be applied to insure safe handling of waste:

A. The container must be very clearly labeled with the solution name (**no abbreviation, no formulas**).

B. The composition of the solution must be displayed. Only solutions with the same ratio $H_2SO_4/30\%H_2O_2$ should be present in a same waste container.

C. The label must also include very visible warning signs in order to avoid the addition of any other types of chemicals (including traces of organics, photoresist, water ...).

D. **Maintain a log of all additions to Piranha waste bottles, displaying dates, amount, swirling procedures (if applied).**

E. **The last addition should be no later than 3 months after the first addition.**



b) Spills

Only employees trained in the handling of Piranha solutions should clean up spills. In the event of a small spill:

1. Notify personnel from the immediate area to stay away from area.
2. Wear appropriate PPE to clean spill.
3. If spill kit is present, use acid or base neutralizing material to neutralize Piranha solution. Test with litmus paper or colour-indicating solution until the spilled material is within the neutral range of pH 6-8.
4. Clean the area with inert absorbent materials (vermiculite, dry sand, oil-sorb, or kitty litter). Do not use combustible organic materials (e.g., spill pads, paper towels, unless the spilled material is properly neutralized). The area should be soaked with detergent, then rinsed with water. Discard contaminated materials in hazardous waste containers, labelled and clearly identified.
5. Advise your supervisor and complete an incident report.

In the event of a large spill located outside a chemical fume hood:

1. Advise and warn co-workers.
2. Evacuate the area immediately.
3. Restrict the access to the area.
4. Notify Campus Safety and Prevention Services (CSPS) at **3717** or **514 848-3717**, providing them with the following information:
 - a. Location of the spill
 - b. Name of hazardous material
 - c. Quantity involved
 - d. Related health risks and precautions to be taken
5. Provide the Safety Data Sheets (SDS) or appropriate documentation.

7. Emergency Procedures

a) Skin Contact

1. Remove contaminated clothing and immediately wash the affected area with large amounts of water until all evidence of the chemical has been removed (approximately 15 minutes).
2. Call CSPA at **3717** for emergency medical assistance.

b) Eye Contact

1. Immediately wash the affected eye with large amounts of water until all evidence of the chemical has been removed (approximately 15 minutes).
2. Do not allow the victim to rub or keep eyes closed.
3. Call CSPA at **3717** for emergency medical assistance.

c) Inhalation

1. Immediately move the victim to fresh air.
2. Call CSPA at **3717** and ask for medical assistance; seek medical attention in the event of respiratory irritation, cough, or tightness in the chest. Symptoms may be delayed.

d) Ingestion

Not a likely route of exposure.

In all cases of exposures, a copy of the Safety Data Sheet (SDS) of the different components must be brought to the emergency room as the treating physician might be unaware of the treatment measures for Piranha solution. All Piranha solution incidents must be reported to your Supervisor and to Environmental Health & Safety. An [injury/near-miss report](#) must be filled for any incident involving a Piranha solution spill or exposure.

If you have any concerns about the use of Piranha solution at Concordia University, please contact EHS at ehs@concordia.ca.

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Revision dates: November 2016, July 2024

References (updated in July 2024):

- SDSs: Fisher Scientific Sulfuric Acid (concentrated) [SDS](#); Fisher Scientific Hydrogen Peroxide (20-35%) [SDS](#); Fisher Scientific Ammonium Hydroxide (25-30%) [SDS](#).
- Stabilized Nano-Strip® formulation [SDS](#).
- Schmidt, H. G. Safe Piranhas: A Review of Methods and Protocols, *ACS Chem. Health Saf.* **2022**, *29*, 54-61. <https://doi.org/10.1021/acs.chas.1c00094>.
- Zhang, B.; Zhang, L.; Wang, H.; Wang, X. Lessons learned from the explosion that occurred during the synthesis of Diaminomethanesulfonic Acid: Discussion and Preventive Strategies, *ACS Chem. Health Saf.* **2021**, *28*, 244-249. <https://doi.org/10.1021/acs.chas.1c00021>.
- The University of Akron, College of Polymer Science and Polymer Engineering – Lessons Learned: [Piranha solution Near Miss](#) – Consulted in July 2024.
- Harvard University: [Laboratory Safety Guideline – Piranha Solution](#) (updated on May 24th, 2024) – Consulted in July 2024.
- University of Toronto – Chemistry Department, Lash Miller Laboratories St. George Campus: [Piranha Solution](#) – Consulted in July 2024.
- University of British Columbia Safety & Risk Services: [Working Safely with Piranha Solution](#) – Consulted in July 2024.
- Chandra, T.; Zebrowski, J. P.; McClain, R.; Lenertz, L. Y. Generating Standard Operating Procedures for the manipulation of hazardous chemicals in academic laboratories. *ACS Chem. Health Saf.* **2021**, *28*, 19-24. <https://dx.doi.org/10.1021/acs.chas.0c00092>.