# C8. Handling Piranha Solution

*Work with Piranha solution requires prior approval*

## BACKGROUND

### Piranha Solution

Piranha Solution (or piranha etch) is a strong oxidizing agent that removes most organic residues off substrates. Acid piranha is usually a 3:1 mixture of concentrated Sulfuric acid with 30% hydrogen peroxide. Piranha solution should only be used when less aggressive cleaning methods fail. All persons working with Piranha solution must be aware of the hazards, know the details of this SOP and be trained in proper use, disposal, and emergency procedures. Obtain approval from Health, Safety & Environment (HSE) prior to starting work with piranha solution.

**Piranha solutions are extremely energetic and may result in explosion or injury resulting from chemical and thermal burns if not handled with extreme caution.**

### Safer Alternatives

Elimination, followed by substitution are the top two tiers of the hierarchy of controls. Where elimination isn't feasible, substitution takes precedence. Two substitutes for Piranha are:

- NoChromix
- Nanostrip

Both of these are more stable than Piranha solution. Should the decision to use Piranha solution still be made, diligent safety planning must encompass the entire Piranha lifecycle from preparation to disposal. This document can serve as an initial step toward developing a department or lab specific Safe Work Procedure (SWP).

## HAZARD

Extremely corrosive to organic material. Direct contact will burn skin and be extremely corrosive to mucous membranes, upper respiratory tract, and serious eye damage. Both liquid and vapor phases are extremely corrosive to skin and respiratory tract.

Very strong oxidizer when in contact with organic compounds. Extremely energetic and exothermic, which may result in explosion if not handled carefully. Solutions made using hydrogen peroxide at concentrations greater than 50% may cause an explosion. Dissolving a large amount of organic contaminant will cause violent bubbling and a release of gas that can cause an explosion.

Do not breathe dust/fume/gas/mist/vapors/spray. May irritate the respiratory tract if vapor is inhaled. May cause cancer.

## RESPONSIBILITY

### Employer

All work must be pre-approved by the Principal Investigator (PI) prior to use. PIs are required to provide all PPE and safety training specific to each solution and method of use.

### Employee

Must be aware of the hazards, know the details of this SOP and be fully trained and signed off in the proper use, disposal, and emergency procedures before starting work.

## TRAINING REQUIRED

Training must include:

- Chemical Safety Course (https://wpl.ubc.ca/browse/ubcohse/courses/wpl-srs-chem)
- Documented specific training on the techniques and processes to be used
- Reading and understanding of the relevant Safety Data Sheets (SDS)
- Demonstrated competence to perform the work
- Orientation to the location and use of the nearest eye wash and safety shower stations

A review of the Safe Work Procedure (SWP) and re-approval is required when there are any changes to procedures, personnel, equipment, or when an incident or near-miss occurs.

## HAZARD CONTROLS

### Engineering / Ventilation Controls

- To prevent buildup of explosive gases, all Piranha work should be performed in an annually certified chemical fume hood.
- The fume hood with the sash must be kept at the certified position or lower. Verify the fume hood is “on” before using it and functioning as designed (hold a light piece of tissue paper at the interface to observe flow).
- If a fume hood is not available for this work, an appropriate respirator must be used by the person preparing / using the solution and by all people present in the room where the solution is prepared and handled.
- The nearest emergency eyewash should be within 10 seconds from the area of work, and should be checked weekly for proper functioning.

### Personal Protective Equipment (PPE)

- Eye Protection: at a minimum, safety goggles (not glasses) must be used. A combination of safety goggles and face shield is recommended.
- Skin and Body Protection: wear a chemical resistant lab coat, long pants, and closed-toed shoes. A chemical resistant Neoprene apron must be worn on top of the lab coat.
- Hand Protection: Regular nitrile gloves do not provide sufficient protection. Heavy duty neoprene or butyl rubber gloves must be worn. It is recommended that legs should also be covered by wearing a full size chemically resistant suit.

- Respiratory Protection: a ½ face elastomeric respirator fitted with corrosive organic vapors cartridges must be used when there is no engineering control available (fume hood). Respirators must be fit tested prior to use. Information on Respiratory Protection can be found on the HSE website, or by taking the Respirator Fit Testing course.

## MATERIALS NEEDED

| Chemicals | Equipment | |
|---|---|---|
| - Concentrated sulfuric acid ($H_2SO_4$) | - Stir place and stir bar | - Stainless steel tweezers |
| - 30% hydrogen peroxide ($H_2O_2$) | - Secondary container | - Pyrex funnel |
| - Sodium bicarbonate ($NaHCO_3$) | - Glass beaker | - Paper towels |
| | - Graduated Cylinder | - pH paper |
| | - Watch glass | - Spray water bottle |
| | - Dedicated glass waste bottle with vented cap | - Spill kit |

## SAFE WORK PROCEDURE

### Pre-Preparation

Piranha solutions should be made at its point of use, in the quantity needed for that time, and **not** transported or stored.

1. Always make sure there is another person in the room with you when you make piranha solution. This person must have the training allowing to assist if necessary.
2. Remove as much organic material from substrate as possible by following the pre-piranha procedure (15 min sonication in Hellmanex, 15 min sonication in acetone, 15 min sonication in isopropanol). Thoroughly rinse substrate at least three times and store in distilled water (even trace amounts of organic acids, bases and organic solvents will react violently with piranha solution).
3. Ensure fume hood is on and empty of all other chemicals. Do not proceed if any organic or basic chemicals are in the fume hood. Place warning sign on fume hood.
4. Verify that appropriate spill cleanup materials and neutralizers are available.
5. Wear goggles, face shield, apron, and acid resistant gloves. Rinse gloves before and after use.
6. Wipe down the fume hood with distilled water and paper towel.
7. The concentration of hydrogen peroxide solution used should be, at most, 30%, never use a higher concentration of hydrogen peroxide as an explosion may occur.
8. Piranha solution is active only if freshly prepared. Prepare small amounts of solution to be used for each application.

**Preparing the Acid Piranha Solution (procedure for 100 mL 3:1 solution)**

1. All steps (1 to 10) below will be done inside a working fume hood
2. Place a glass beaker into a secondary container (e.g. glass deep evaporating dish) and both onto a magnetic stir plate. Beaker should be 3-4 times the volume of volume of Piranha solution being prepared to have adequate room for bubbling.
3. Place a magnetic stir bar inside the beaker
4. Add 75 mL of concentrated sulfuric acid (measure with a 100 mL graduated cylinder) then power ON the magnetic stir plate
5. SLOWLY add 25 mL of 30% hydrogen peroxide, with gentle stirring. Always slowly add the peroxide to the sulfuric acid. Add the peroxide slowly as the reaction very exothermic; the solution may bubble and heat up to 120°C.
6. Stir and allow for the solution to react for a few minutes and reach a high temperature before immersing substrate to be cleaned.
7. Carefully submerge your substrate in the Piranha solution. Only use stainless steel tweezers when handling items immersed in piranha.
8. Cover the solution with a watch glass (leave room for vapor to escape) and let sit for 45 minutes. Stirring or manual scrubbing is not required during this step.
9. When there is no longer evidence of a reaction happening, carefully remove your substrate from the Piranha solution into a beaker of distilled water (inside the fume hood).
10. Thoroughly rinse substrate at least three times with distilled water.
11. Decontaminate all equipment before removing from the designated area: wash all glassware well. Wipe down the fume hood with distilled water and paper towel
12. Rinse off the acid resistant gloves. Remove PPE, wash hands and arms with soap and water.

**Acid Piranha Solution waste disposal**

<u>Hazardous Waste</u>

1. Allow hot piranha solution to cool down, put the waste solution in the already prepared cleaned, dried, and labelled glass waste bottle with a vented cap. Use a Pyrex funnel if needed.
    a. Never fill the waste container more than 3/4 full.
    b. Always ensure there is an exhaust hole at the top of the container (vented cap) to prevent pressure buildup from vapors (you can request vented caps from HSE through the Hazardous Waste Inventory System)
    c. Never dispose of any other chemicals in the piranha waste container
    d. Clearly label the waste bottle “Piranha Waste Only– do not add any other waste”
    e. Store in secondary containment
2. Submit a request (via the Hazardous Waste Inventory System) to dispose of the waste as hazardous waste.
    a. Find the entry “concentrated sulfuric acid and hydrogen peroxide 30%, mixture 3:1 (piranha solution)” in the HWIS
    b. Keep track of the date when the solution was initially prepared – you will need it for submission. Piranha waste should not be stored for over 3 months.
    c. Replace vented cap with regular cap before waste is picked-up

Neutralization – should only be done for volumes less or equal to 100 mL of piranha waste

1. Allow used hot piranha solution to cool down (overnight, or for 24 hours)
2. Use a large beaker (see calculations below), stir bar and stir plate
3. With a spatula, slowly add sodium bicarbonate (NaHCO3) to the used piranha solution
    a. You will need 2 moles of NaHCO3 for each mole of H2SO4 (e.g. to neutralize 75 mL conc H2SO4 you will need about 227 g NaHCO3)
    b. Sodium bicarbonate will cause rapid gas release and bubbling as it reacts with the sulfuric acid. Ensure gas release significantly slows down before adding more bicarbonate.
    c. After no more bubbling is observed with addition of the bicarbonate, use pH paper to test the pH of the solution. Aim for a pH in the range 6-10.
4. Allow the solution to cool overnight in the fume hood – do not cover the beaker.
5. The neutralized solution can be disposed of down the sink, under running water.

**Emergency Procedures**

Spill Response – use acid neutralizing material to neutralize piranha solution, test with pH paper until spill is in the 6-8 pH range. Do **not** use paper towels, rags or sawdust because such materials may spontaneously ignite. Place residue inside a piranha solution waste container, label, and arrange for chemical waste pick-up.
In case of large spills (>100 mL) evacuate the area and call UBC security at 250-807-8111 and/or 911 for assistance.

Personal exposure – Piranha solution is extremely corrosive to skin and eyes. In case of contact with skin or eyes, wash the affected area with water for at least 15 minutes. Call UBC security (at 250-807-8111) and/or 911. In case of exposure by inhalation, remove the person to fresh air and seek medical attention.
Always report spill and/or personal exposures in UBC Centralized Accident/Incident Reporting System (CAIRS).

## RESOURCES

Schmidt, H. G. (2022;2021;). Safe piranhas: A review of methods and protocols. Journal of Chemical Health & Safety (Online), 29(1), 54-61. https://doi.org/10.1021/acs.chas.1c00094

## DOCUMENT INFORMATION

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