Procedure on handling and using Piranha solution

Piranha solution, also known as piranha-etch, is extremely energetic and potentially very dangerous, being both strongly acidic and a strong oxidizer. Piranha solution has been responsible for a number of serious incidents in R&D laboratories. Therefore, before using Piranha solution you should try alternative safer methods.

Traditional Piranha solution is a 3:1 mixture1 of sulfuric acid (H_2SO_4) and 30% hydrogen peroxide (H_2O_2), 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). [NOTE: Several different mixture ratios are commonly used, and all are called piranha. The typical mixture is 3:1. Other protocols may use a 4:1 or even a 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. All 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 to initiate the reaction.]

Mixing the solution is exothermic. The resultant heat can bring solution temperatures up to 120°C. You 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.

Piranha solution can cause explosions. NEVER put Piranha solution in closed containers as explosions can occur due to gas generation and consequential over pressurization. Explosions may also occur when Piranha reacts with organic material or if the peroxide solution concentration is more than 50%. Therefore the peroxide **must** always be added to the sulphuric acid, NEVER vice versa.

Due to its extreme hazards, before you work with Piranha solution, you should consider less hazardous alternatives. However, if it is necessary to use Piranha solution you MUST:

1. Obtain approval from you Principal Investigator (PI) before using Piranha solution.
2. Complete a Hazardous Substance Risk Assessment to identify appropriate control measures for YOUR procedure including the hazards and risks of handling Piranha solution, how to control exposure and respond to emergency situations.

3. Inform any others working in the area that you are handling Piranha solution and the hazards it represents and label your work area using the appropriate signage. (Please refer to annexure)

4. Not work in isolation, as with any hazardous substance, those working with Piranha solution should not work alone i.e., there should be someone within sight or calling distance at all times.

5. Ensure the area where Piranha solution is handled has a spill kit with acid-neutralizing material to neutralize potential accidental spills.

Safe handling procedures

Do not store Piranha solution. Mix a fresh solution for each use.

1. All work involving Piranha solution MUST be conducted inside a fume cupboard.
   a. Wherever reasonably practicable, the fume cupboard sash should be between you and the Piranha solution
   b. No other work should be carried out in the fume cupboard whilst Piranha is present
   c. Do not move Piranha solution from the fume cupboard where it was made
2. Personal Protective Equipment (PPE) should include:
   a. Safety glasses and face shield
   b. Cotton based lab coat, with pop-stud fasteners to facilitate rapid removal
   c. Thick chemically resistant gloves (disposable Nitrile gloves will not provide sufficient protection) – check for pinholes in gloves before putting them on
   d. An acid resistant apron when handling significant quantities i.e. greater than 100mls
3. Open-toed shoes should not be worn and bare legs should be covered.
4. Piranha solution should be handled in glass or Pyrex containers. Secondary containment is advisable e.g., glass crystallising pans. Piranha solution is not compatible with plastic.
5. Containers used during the experiment must be clearly labelled and a warning sign must be displayed on the fume cupboard to indicate the use of Piranha solution (see Appendix 2).
6. Always add hydrogen peroxide to sulfuric acid slowly with gentle stirring. Never vice versa.
7. The hydrogen peroxide component should be kept to below 30%, never to exceed 50%.
8. Mixing the Piranha solution can raise the temperature to 120°C, the solution will typically bubble vigorously as it approaches 100°C.
9. You must always leave the solution to cool to a reasonable temperature before handling.
   a. Handling hot containers increases the risk of spillage

b. Once the mixture has stabilised it can be further heated to sustain its reactivity

c. Premature heating can result in rapid temperature rises and excessive boiling

d. If heating, always use a hot plate with stir capability that incorporates over temperature protection to prevent overheating

10. Depending upon use, it is possible to mix Piranha solution before application or it can be directly applied to the material, applying the sulfuric acid first, followed by the peroxide.

11. Do not mix Piranha solution with incompatible materials such as organic acids, organic solvents, organic material (e.g., plastic and nylon) and bases (photoresist is a strong base).

12. Ensure containers and substrates are rinsed and **dried** before coming into contact with Piranha solution (Piranha solution is only used to remove **residues**, NOT the compounds).

13. Adding anything to the Piranha solution must be done slowly and carefully, giving the solution time to stabilise and to prevent thermal shock to the item.

14. Hot, active Piranha solution that is no longer being used should never be left unattended.

15. After use, allow the solution to cool down for several hours in an open container in the fume cupboard, preferably leaving overnight, allowing oxygen gas to dissipate, before disposal.

16. **Do not seal containers containing Piranha solution, as** Oxygen given off during the self-decomposition of Piranha solution, as well as any oxidation products of organic compounds can cause the container to explode.

Emergency procedures

All contaminated clothing should be removed immediately. Those assisting should wear appropriate PPE (safety glasses, gloves and lab coat/apron).

1. ***In case of skin contact***: May cause skin burns. Flush the skin with copious amounts of water for at least 15 minutes. Seek medical attention.

2. ***In case of eye contact***: Piranha solution is extremely 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.

3. ***In case of inhalation***: 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.

4. ***In case of ingestion***: Not a likely route of exposure.

Spillages should be absorbed with acid-neutralizing material. Double bag the spill waste in labelled clear plastic bags for disposal as hazardous waste.

Piranha solution waste disposal

Due to the hazardous nature of this material, in particular the potential for gas generation and over-pressurisation of a container when the solution is still hot, the following procedure must be adhered to.

1. Cool the solution to room temperature in a clearly labelled open container for several hours (preferably overnight) in the fume cupboard. Ensure adequate signage on the fume cupboard to indicate the presence of Piranha solution overnight.

2. Put 5 times as much ice as the amount of solution you want to neutralize into a container large enough to hold the ice, the piranha and the neutralizing solution (e.g. 500 g of ice for 100 mL of 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. The properly neutralized waste solution can be disposed as waste water in drainage or as Non-Halogenated waste. [Reference: https://www.drs.illinois.edu/SafetyLibrary/PiranhaSolutions]

2. Slowly dilute 1 in 10 with water using clean glassware and a stirrer (i.e. 100 ml Piranha solution into 1 litre of water). Having pre-flushed the sink and drain-pipe with water dispose of the 1 in 10 diluted solution to the drain with copious amounts of water.

A classic lab accident with Piranha solution

A group of researchers regularly cleaned their glass sinter funnels by running Piranha solution through them (using ‘house vacuum’) into a filter flask. One day a researcher made the mistake of leaving a trace of acetone in the flask. When the Piranha solution hit the acetone, it exploded and numerous pieces of glass embedded themselves into the researcher’s face. Luckily they were wearing their safety glasses or they would probably have been blinded.

Read this account of the incident and then ask yourself whether a clean sinter funnel is worth this:

The explosion was heard from two labs away. The first person on the scene found the student on the floor halfway across the room surrounded by a large pool of blood. The filter flask had turned to dust; the largest fragment being about 2 mm even though it had been wrapped in heavy black electrical tape. The metal 3 prong clamp that held the flask had sheared off at the point where it was clamped to the latticework in the fume cupboard. A row of glass cabinets along one wall were peppered with holes from the shrapnel. A glass drainpipe on the wall opposite the fume cupboard (about 8-10 m away) was cracked in the middle. It is believed that it wasn't caused by shrapnel, but by the compression wave of the blast.

The student had been wearing rubber gloves, a thick sweater, a lab coat, an apron and safety glasses at the time of the explosion. The fume cupboard sash was partially down and absorbed some of the blast preventing the student from catching all of it in the face. The arm holding the sinter funnel received most of the damage -- the glove was completely flayed and their arm had several hundred small bits of glass embedded in it as well as several fairly large lacerations. They had a wound about 20 mm in diameter just next to their jugular vein. At least one piece of glass went through their cheek. The student (and everything else) was also covered with hydrogen peroxide and sulfuric acid; something that wasn't realized until much later because those first on the scene had no way of knowing what had happened.

The student spent the next six hours having tiny bits of glass picked out of their arm, neck and face. The remaining pieces of glass worked their way out of the skin over several weeks. The student also had some nerve/tendon damage.

Now consider this: 10 minutes later and the rest of the research group would have left for dinner. The student was working ALONE in the laboratory, 'just cleaning up'. Maybe they could have got to a phone on their own however, when discovered the student was trying to get up, but not very successfully. Ever tried to stand up in a pool of your own blood and sulfuric acid on a laboratory floor while dazed and injured? Think about that the next time you are working alone.

PIRANHA SOLUTION IN USE

PIRANHA SOLUTION IS A MIXTURE OF CONCENTRATED SULPHURIC ACID AND HYDROGEN PEROXIDE
IT IS HIGHLY CORROSIVE AND A STRONG OXIDISER WITH THE POTENTIAL TO CAUSE AN EXPLOSION IN A SEALED CONTAINER OR IN CONTACT WITH ORGANIC MATERIAL

DO NOT DISTURB

Research Group:
User:
Date:

Content of this draft is adapted from

www.ch.cam.ac.uk *(Department of Chemistry, University of Cambridge)*