

Chemical Safety Guidance Series

February 2020

# Acid Piranha Solution: User Guidance

Occupational Health & Safety Service

HSD176C (rev 3)



UNIVERSITY OF  
CAMBRIDGE

## Guidance for Using Acid 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 (see Appendix 1). Therefore, before using Piranha solution you should try alternative safer methods.

Traditional Piranha solution is a 3:1 mixture<sup>1</sup> of sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and 30% hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), 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).

**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. (Note: Only those deemed competent to do so by the PI should be allowed to work unsupervised with 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 (see Appendix 2).
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. Restrict the use of Piranha solution to Departmental 'core hours', e.g. typically between 09:00 and 17:00, Monday to Friday.
6. Ensure the area where Piranha solution is handled has a spill kit with acid-neutralizing material to neutralize potential accidental spills.

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<sup>1</sup> Several different mixture ratios are commonly used, and all are called piranha. The typical mixture is 3:1 sulfuric acid : hydrogen peroxide. Other protocols may use a 4:1 or even a 7:1 mixture. A closely related mixture called 'base piranha', is a 3:1 mixture of ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) with hydrogen peroxide. Base Piranha, also known as 'TL1 cleaning', is NOT specifically covered by this guidance, however many of the precautions would still be applicable since all are equally dangerous when hot. However the reaction in the acid piranha is self-starting whereas the base piranha must be heated to 60°C to initiate the reaction.

## 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 bulk 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.

### Do not seal containers containing Piranha solution<sup>2</sup>.

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<sup>2</sup> Oxygen given off during the self-decomposition of Piranha solution, as well as any gases 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. Dilute the Piranha solution in a fume cupboard, by adding it slowly to water (1 in 10) using clean glassware and a stirrer (i.e. 100 ml Piranha solution into 1 litre of water).
3. Having extensively pre-flushed the sink and drain-pipe with tap water, dispose of the 1 in 10 diluted solution to the drain with copious amounts of water.
4. Rinse out glassware and flush to drain

**DO NOT STORE PIRANHA SOLUTION: DISPOSE OF AS SOON AS SAFE TO DO SO**

## Publication history

First published September 2011, reviewed without significant change in 2014, 2016 and 2020.

## Appendix 1: 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?

**Please think about these issues the next time you are thinking of working alone with any hazardous substance, let alone something as potentially dangerous as Piranha solution.**

## Appendix 2: Signage

|                                                                                                                                                                                                                                                                                               |                                    |                                                                                     |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------|-------------------------------------------------------------------------------------|
|                                                                                                                                                                                                              | <b>PIRANHA SOLUTION<br/>IN USE</b> |  |
| <p>PIRANHA SOLUTION IS A MIXTURE OF CONCENTRATED<br/>SULPHURIC ACID AND HYDROGEN PEROXIDE</p> <p>IT IS HIGHLY CORROSIVE AND A STRONG OXIDISER<br/>WITH THE POTENTIAL TO CAUSE AN EXPLOSION IN A<br/>SEALED CONTAINER OR IN CONTACT WITH ORGANIC<br/>MATERIAL</p> <p><b>DO NOT DISTURB</b></p> |                                    |                                                                                     |
| In the event of an emergency contact:                                                                                                                                                                                                                                                         |                                    |                                                                                     |
| Researcher:                                                                                                                                                                                                                                                                                   | Tel:                               |                                                                                     |
| Supervisor:                                                                                                                                                                                                                                                                                   | Tel:                               |                                                                                     |
| Additional information:                                                                                                                                                                                                                                                                       |                                    |                                                                                     |



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