

## **Special Code of Practice L: Guidance on the use of Piranha Solution (Hydrogen Peroxide/Sulphuric Acid Mixtures)**

Before using Piranha solution or Caro's acid you should consider alternative methods that are safer.

### General Points

1. Piranha solution is a mixture (typically 3:1 v/v) of concentrated sulphuric acid with 30% hydrogen peroxide used for cleaning and/or hydroxylating inorganic surfaces. It is potentially very dangerous, being both strongly acidic and strongly oxidising. Caro's acid,  $\text{H}_2\text{SO}_5$ , can be also be prepared by the reaction of concentrated sulphuric acid with aqueous hydrogen peroxide.
2. **NEVER put Piranha solution in closed containers as explosions can occur due to gas generation and consequential over pressurisation.** 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, with stirring, NEVER vice versa.**
3. Piranha solution should be handled in clean glass or Pyrex containers. Secondary containment is advisable e.g. a glass petri dish. **Piranha solution is not compatible with plastic.** Do not mix Piranha solution with incompatible materials such as organic acids, organic solvents, organic material (e.g. plastic and nylon) and bases.
4. Only use glass stirring rods, do not use metal or plastic spatulas.
5. Assess the minimum quantity of solution that is needed for the cleaning/surface activation process. Do not prepare excessive amounts of solution. A full risk assessment should be made in the laboratory notebook.

### Preparation of Piranha Solution

1. All work involving Piranha solution **MUST** be conducted inside a fume cupboard. No other work should be carried out in the same fume cupboard. Piranha solution should not be moved from the fume cupboard in which it is made.
2. A warning sign should be displayed on the fume cupboard to indicate the use of Piranha solution..
3. Ideally, the work should be conducted behind a secondary blast screen. If this is impractical, the researcher preparing the solution **MUST** wear a face shield **IN ADDITION TO** the safety glasses (EN 166-F) specified by the Departmental safety policy. Other PPE required includes a lab coat (and optional acid apron) and gloves that cover the wrist and meet the EN 374-3

specification, with resistance to sulphuric acid and hydrogen peroxide. Butyl rubber and Viton are examples of suitable glove materials; some nitrile gloves such as Sol-Vex® 37-900 are also appropriate.

4. Mixing hydrogen peroxide and sulphuric acid is an exothermic process. 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.
5. Add hydrogen peroxide to sulphuric acid slowly with gentle stirring.
6. The hydrogen peroxide component should be kept to below 30%, and must never exceed 50%.
7. The temperature can increase to 120 °C whilst mixing Piranha solution, and the solution will typically bubble vigorously as it approaches 100 °C. You must always leave the solution to cool to a reasonable temperature before handling.
8. Once the mixture has stabilised it can be further heated to sustain its reactivity. Premature heating can result in rapid temperature rises and excessive boiling. If heating, always use a stirrer hot plate with temperature protection to prevent overheating.
9. Hot, active Piranha solution that is no longer being used **should never be left unattended**.

#### Use of Piranha Solution

1. 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).
2. 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.
3. 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.
4. Dilute the Piranha solution in a fume cupboard, by adding it slowly to ice-water (1 in 10) using clean glassware and a glass stirrer (*i.e.* 100 ml Piranha solution into at least 1 litre of ice-water).
5. If a large volume of acid has been prepared, < 100 ml, the diluted Pirhana solution should be neutralised by the slow, portionwise addition of sodium hydrogen carbonate.

6. 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.
7. Glassware should be flushed out with copious amounts of water and disposed down the drain.
8. Piranha solution MUST NOT be stored, but disposed of as soon as it is safe to do so.

### Emergency Procedures

**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.

**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.

**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.

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

Prof A. Beeby  
14 September 2019

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This section is to be completed electronically, and then the PDF sent by email to [chem.safety@durham.ac.uk](mailto:chem.safety@durham.ac.uk).

### UNIVERSITY OF DURHAM - DEPARTMENT OF CHEMISTRY

I have consulted with Prof. Beeby, read the notes of guidance for users of Piranha and retain a copy for reference. I agree to follow their recommendations.

Signed:

Date:

Name:

Email address: