University of St Andrews

Safe Use of Piranha Solution

1. Introduction

Piranha solutions are a mixture of concentrated sulphuric acid with hydrogen peroxide, usually in a ratio of 3:1. Piranha solution should only be used to clean organic residues in trace amounts. It should not be used if a large amount of organic material is present as it may react explosively. The mixing procedure is a highly exothermic reaction that can reach temperatures of 100 °C or higher. The reaction of hydrogen peroxide on concentrated sulfuric acid produces highly activated and oxidizing peroxymonosulfuric acid (H_2SO_5), also called Caro's acid (corrosive, oxidising, and explosive).

Piranha solution is a last resort for cleaning glassware and should only be used when safer alternatives have been exhausted (e.g. dilute nitric acid, conc. nitric acid or aqua regia)

2. Preparation

Before Working with Piranha Solution:

- Ensure the glassware to be cleaned was last washed with water and is dry
- Clear the fume cupboard of any organic solvents and reagents
- Only use piranha solution during normal working hours with at least one other person in the lab
- Inform other lab users that piranha solution is use
- Make sure you know the location of the nearest eyewash station in case of contact with eye

3. Best Practice

When Working with Piranha Solution:

- Full PPE should be worn at all times (during preparation, use and disposal). A Laboratory coat, thick gloves (e.g. marigolds) and a full-face shield must be worn
- Only prepare the amount you need and do not attempt to store
- Any batch made over 100 mL requires cooling in an ice bath when mixed
- Hydrogen peroxide concentrations should be kept below 30%
- Always use Pyrex glass containers. Piranha solution will degrade plastic
- Have a pre-prepared solution of dilute aqueous $NaHCO_3$ or $CaCO_3$ ready in case of small spillages

Always add the hydrogen peroxide to the sulphuric acid very slowly.
DO NOT ADD SULPHURIC ACID TO HYDROGEN PEROXIDE.

4. Example Procedure

In a properly functioning fume cupboard, to glassware that contains no organic material or solvent, was added sulphuric acid (Corrosive - Avoid direct contact) followed by hydrogen peroxide (Corrosive and explosive - Avoid direct contact and sources of ignition) in a 3:1 ratio and the solution is stirred with a glass rod. (CAUTION: will self-heat to boil).

The piranha solution is added to unclean glassware to remove organic contaminants (CAUTION: This is likely to release CO_2). The glassware will not be sealed throughout the process and labelled clearly.

Once the cleaning procedure is complete, the piranha solution is allowed to cool to room temperature. The clean glassware will be thoroughly rinsed with water and, if used to clean glass frits, a large volume of water will be passed through the frit via gravity to ensure trace piranha solution has been removed. The water rinsed glassware can then be washed with acetone.

5. Emergency Response

5.1 Small Spillage of Piranha Solution

In the event of a small spillage of piranha solution, **DO NOT** attempt to mop up the spill with paper towels as they may spontaneously ignite. Instead carefully neutralise the spill with dilute aqueous $NaHCO_3$ or $CaCO_3$ (keep this nearby) and check pH is within safe range (6-8) before mopping up with paper towels.

5.2 In Case of Skin Contact

Flush the skin with copious amounts of water for at least 20 minutes. Send another lab user to inform First Aider.

5.3 In Case of Eye Contact

Use an eyewash station immediately to flush contaminated eye(s) for at least 20 minutes. Send another lab user to inform First Aider.

5.4 In Case of Inhalation

Conscious persons should be assisted to fresh air. Seek medical attention if an exposure is suspected. Symptoms included respiratory irritation, cough, or tightness in the chest. Symptoms may be delayed.

6. Disposal Procedure

Place five times as much ice as the amount of the solution you want to neutralize into a glass container large enough to hold the ice, the piranha and the neutralizing solution (e.g., use 500 g of ice for 100 ml 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 neutralised solution can then be disposed of down the sink with copious amounts of water.