Use and Disposal of Acidic 'Piranha' Solutions

Incidents involving the use and disposal of acidic 'piranha' solutions indicate a heightened potential for serious injury to campus researchers, EH&S staff and staff of the hazardous waste disposal vendor handling piranha wastes for final disposal. As a result, increased safety procedures are required.

<u>Piranha solutions should only be used when there are no other alternatives.</u> Due to the difficulties in handling and disposing of piranha, along with the significant safety hazards it presents in the laboratory, it should not be used for routine cleaning of glassware or anything else. <u>Substitutes such as NanostripTM or a</u> <u>NochromixTM solution are safer alternatives and present less difficulty in disposing</u>.

2014 Update: **Due to reduced risks associated with the use and disposal of Nanostrip, labs that use Nanostrip exclusively instead of piranha can be exempted from the EH&S SOP requirements for piranha solutions. There are a few labs on campus that have stopped using piranha and switched to Nanostrip. Here are some of the benefits these labs describe in using Nanostrip: "It is premixed – no dangerous mixing required", "It has predictable/consistent etching results", and "It allows for multiple reuses". Nanostrip is more stable than piranha and contains very little hydrogen peroxide when compared with piranha solution. However, Nanostrip must be handled with the same precautions as piranha while in the lab; including the use of vented caps for wastes, designating specific areas of the lab for use, signage, etc.**

Principle Investigators are responsible for developing safe procedures for using piranha that are specific to their laboratory and also ensuring that each individual in their research group is trained on these procedures prior to using piranha. This training should also include emergency splash/spill procedures.

Piranha should never be used or be handled by individuals working alone in the laboratory. **The use of piranha should be restricted to normal business hours during the work week.** As with any other strong acid, precautionary safety measures include: acid resistant gloves, chemical splash goggles, lab coat and other protective clothing; used only in a chemical fume hood and within the vicinity of emergency eyewash and safety shower; provide secondary containment; segregate from all other materials and wastes.

Piranha should be used only as a final clean of substrates which have previously been cleaned and scrubbed of significant organics or metals contamination. The substrates must also be thoroughly rinsed of any cleaning agents/detergents before submersion in piranha occurs. Piranha solution can become unstable and very dangerous if there is a significant accumulation of organic compounds or certain metals, and disposal options of such a solution are extremely limited.

Every laboratory that uses piranha should have a spill cleanup/acid neutralizing kit available for use. In the event of a small piranha spill, neutralize with sodium bicarbonate or other acid neutralizer and soak up with an inorganic-based absorbent if possible. If an organic-based absorbent such as paper towels must be used, place them in a tightly sealed plastic bag to keep them wet with water; such materials may spontaneously ignite if dried. The best fire extinguishing agent is water. In the event of a piranha spill that is beyond your means to safely remediate call EH&S at 303-492-6025 for assistance. For spills that are immediately dangerous to life and health follow the procedures outlined in your emergency contingency plan and call 911.

It is important to remember that all used piranha solutions contain some level of hydrogen peroxide that remains after use. Depending on how each piranha solution was used and the amount of time the solution had been kept at an elevated temperature, the amount of hydrogen peroxide remaining could be significant. A

major hazard associated with piranha waste is the off-gassing and pressure generated from the natural decomposition of hydrogen peroxide. This off-gassing, along with the oxidative characteristics of hydrogen peroxide, complicates both transportation and disposal procedures for the hazardous piranha wastes. The natural decomposition of hydrogen peroxide into water and oxygen can take a very long time (1% per year at room temperature). It is important to accommodate for the off-gassing by always storing piranha in an open container during use and cooling – and then in a vented container during storage (EH&S supplies vented caps free of charge, please see disposal procedures below).

To alleviate the hazards associated with transportation of piranha, <u>EH&S will neutralize and drain dispose</u> as much of the piranha wastes as possible within our industrial wastewater treatment facility on campus. As with all other hazardous wastes, it is extremely important to provide accurate information to EH&S related to the concentration of your piranha waste and also of any contaminants present. Each waste bottle of piranha coming into the EH&S facility will be analyzed for remaining hydrogen peroxide content. Wastes containing greater than 10% hydrogen peroxide cannot be treated and will be shipped offsite for disposal.

If it would not interfere with your procedures and can be safely performed within your lab, piranha solution can be carefully heated under controlled conditions and constant supervision. An investigation by EH&S has shown that heating the solution to temperatures of 45-65° Celsius for approximately 1 hour significantly maximizes its intended use and also reduces the hydrogen peroxide content. Heating the piranha solution will prolong its range of effectiveness, reduce overall waste quantities and allow treatment within the EH&S treatment facility. If you would like consultation in this regard please let us know.

We appreciate your cooperation and assistance. EH&S doesn't recommend the use of acid piranha solutions, however it is our intention to provide guidance on the safe use and handling of piranha and also ensure the safe disposal of the wastes with minimal impact to laboratory operations. Ultimately if piranha solutions cannot be safely used and disposed of, its use on campus must be prohibited. We are making our best efforts to avoid that possibility, but we can't do it without the cooperation of the laboratories that use the piranha solutions. Please let us know if you have questions or comments, or need additional assistance.

Here is what Piranha can do in a non-vented bottle:

Ensure this doesn't happen in your lab... Use a vented cap!



Piranha Generation and Disposal Procedures

These procedures must be implemented by all campus labs that use piranha in order to help ensure it can be safely handled and disposed:

- Only pre-approved acid piranha solutions containing Sulfuric acid and Hydrogen Peroxide will be accepted for proper disposal. Piranha solutions that deviate from these ingredients must have disposal arrangements made with EH&S <u>before</u> generation of such solutions occurs. Labs that generate wastes that EH&S cannot handle will be referred to the appropriate hazardous waste disposal vendor for consultation on disposal of their waste. <u>Labs generating</u> <u>such wastes will be directly responsible for all costs associated with such disposal.</u>
- 2. Piranha must be used and stored only inside of a chemical fume hood. The fume hood should have signage posted on the sash warning of the presence and use of piranha. (Example attached on page 4)
- 3. Starting with 30% hydrogen peroxide and 98% sulfuric acid, the mixing ratio should be in a range of 1:5, 1:4 or 1:3 (H₂O₂ : H₂SO₄). Ratios of 1:2 or stronger are not advised and should be managed and stored separately from other piranha waste if you must use them.
- 4. Used piranha solutions must be allowed to cool and off-gas in an open container left inside of a chemical fume hood for 24 hours after use.
- 5. After the initial 24 hours has passed, the cooled piranha solution may be transferred to a piranha waste bottle. When performing the transfer, make sure no heat is produced or reactions are occurring.
- 6. Piranha waste MUST be stored in a glass bottle with a VENTED CAP. EH&S has a supply of vented caps that fit the stock 2.5L sulfuric acid bottles, or other bottles that accept the 38/439 thread cap. EH&S recommends the use of empty sulfuric acid bottles for storing piranha waste. If other bottles are used, laboratory personnel must ensure the vented caps securely fit the bottles prior to adding piranha. Call 303-492-7845 to have some vented caps delivered to your lab. EH&S will not remove piranha waste bottles without vented caps.
- 7. Place signage next to the bottle of piranha waste to warn others of its presence and that it must not be contaminated with any other wastes. (Example attached on page 5)
- 8. Do not over-fill piranha waste bottles. Leave at least 2" of head space in each bottle. Overfilling prevents the vented caps from allowing gas to escape. EH&S will not pick up bottles that are over-filled.
- 9. The outside surface of bottles containing piranha must be completely free of acid residues before the bottles will be picked up for disposal.
- 10. Do not keep piranha wastes on hand for extended periods of time. *The last addition to a piranha waste bottle should be no later than 3 months after the first addition.*
- 11. Each laboratory must establish a Standard Operating Procedure (SOP) for the use of Piranha solution within their laboratory. This SOP must be reviewed by EH&S before piranha wastes will be accepted for disposal. Effective 02/01/2013 EH&S will no longer accept piranha solutions for disposal from a laboratory that has not yet submitted an SOP for the use of Piranha within their laboratory. This SOP will need to be reviewed and approved on an annual basis. Laboratories can submit their SOP to: <u>Ralph.Bogle@colorado.edu</u> for review. (Example SOP attached on page 6)
- 12. A trained lab representative familiar with the processes generating the piranha waste must complete and sign each hazardous material/waste tag for piranha waste.

WARNING Piranha Solution In Use







Piranha Waste

Add no other types of waste!!

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Questions? Contact EHS at (303) 492-6025 or ehs@colorado.edu

EXAMPLE ONLY – Modify with specifics of procedures in your laboratory

Piranha Use and Disposal SOP

- 1. **Do not use or handle piranha solutions while alone in the lab.** Always let someone know that you are working with piranha.
- 2. Use proper Personal Protective Equipment (PPE). Acid resistant gloves, chemical splash goggles, lab coat and other protective clothing.
- 3. **Keep the lab clean and organized.** Know where the eyewash and safety shower are and ensure there is a clear route to them. Use piranha only within a chemical fume hood.
- Manually clean items of organic and metal contaminants with a strong detergent before using piranha. For example, for microscope slides one could use 2% Micro-90 and 18MΩ Millipore water. Rinse well before submersion into piranha.
- 5. **Prepare small quantities** of acid Piranha using 30% reagent grade Hydrogen Peroxide and Sulfuric acid (98%) reagent grade.

The mixing ratio should be in a range of 1:5, 1:4 or 1:3 (H_2O_2 : H_2SO_4). Do not guess on volumes! Always measure the quantity of Hydrogen Peroxide and Sulfuric acid added.

Always add the acid to the hydrogen peroxide solution and not vice versa. Take precaution during the mixing phase as there will be an exothermic reaction.

- 6. Carefully heat the solution. Place the item in the Piranha then use a water bath & heat to 45° 65° Celsius and use for one hour. Sustained temperatures at or above the 45° 65° Celsius range are shown to be more effective at cleaning than just the exothermic heat generated by the solution preparation alone.
- 7. **Cool the waste before adding to the waste container**. Allow the Piranha to cool overnight in an open container (properly labeled) and inside a fume hood (24 hours is suggested) before placing in the piranha waste collection bottle. Slowly add piranha to the collection bottle, and ensure there is no heat generated or reactions occurring. Always use a vented cap on the waste collection bottle!