Between Piranha solution and Chromic acid solution -glass cleaning is a dangerous business

By Kathryn A. Craig

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We all know how important it is to keep laboratory glassware clean and free from contamination. Nobody wants organic or chemical residue to ruin an experiment or potentially cause an injury.

When is it clean enough?

Potassium dichromate ($K_2Cr_2O_7$) is a powerful oxidizing agent and it is, or at least was, the preferred compound for cleaning laboratory glassware of any possible organic residues, lime-scale to unseen miniscule residues. It is used as a saturated solution – in concentrated sulfuric acid – and used very carefully! Spent acid wash is highly toxic and disposal is very expensive. Some histology labs still use this method today.

Piranha solutions are used to remove organic residues from substrates, particularly in microfabrications labs. The traditional piranha solution is a 3:1 mixture of sulfuric acid and 30% hydrogen peroxide.

Potassium Dichromate Acid Baths

Typically potassium dichromate is dissolved in distilled water, then sulfuric acid is slowly added. The conventional method of washing glassware involves soaking glass in a chromic acid-sulfuric acid bath followed by tap water rinses, distilled water rinses, and finally double-distilled water rinses.

One of the procedures I found said "use caution when working with sulfuric acid, add slowly to solution." It then went on to state sulfuric acid fumes are toxic and has target organ effects on skin, respiratory and reproductive systems and fetal tissue.

In case you haven't seen the movie Erin Brockovich lately, here is a list of the potential health effects of working with hexavalent chromium: lung cancer, nasal and sinus cancer, cancers of the trachea and bronchus, non-respiratory cancer. Dermal health effects including irritation, skin ulcers, skin sensitization, allergic contact dermatitis, irritation and ulceration of the nasal mucosa, and perforation of the nasal septum. There are also reports of kidney damage, liver damage, pulmonary congestion and edema, epigastric pain, erosion and discoloration of the teeth, and perforated ear drums.

NIOSH recommends that airborne exposure to all Cr(VI) compounds be limited to a concentration of 0.2 µg Cr(VI)/ m^3 for an 8-hr TWA exposure, during a 40-hr workweek. Is having super clean glassware worth the risk of working with chemicals that have an allowable exposure limit of 0.2 *micrograms*, time weighted average over an 8 hour work day?

Chromic acid is extremely corrosive. One more practical concern with this super-duper glassware cleaning solution is, it will ignite anything ignitable that it comes in contact with -- paper towels, ethanol, and especially random organics in the "waste solvent" can.

Piranha solutions:

Piranha etch is used to remove organic residues from substrates. The standard acid piranha uses a 3:1 mixture of concentrated sulfuric acid (H_2SO_4) with hydrogen peroxide (H_2O_2). Acid piranha is a self-starting reaction and is extremely exothermic; this mixture becomes hot when the hydrogen peroxide is added to the sulfuric acid.

There are many things which will cause the reaction to accelerate. When this reaction is "Out of control", the following can occur: the piranha can foam out of its bin and onto the fume hood deck; this could eventually lead to an explosion. Piranha etch is used to burn organic compounds. If you provide sufficient fuel for them (i.e. photoresist, IPA), they will generate enormous quantities of heat and gas and could lead to an explosion.

Piranha must only be used on glass (preferably Pyrex) containers. Piranha will melt plastics.

When preparing the piranha solution, always add the peroxide to the acid. Piranha

Ultrasonic cleaning is often a good alternative.

solution is very energetic and potentially explosive. It is very likely to become hot, more than 100 degrees C. Piranha stored in a closed container will likely explode.

Adding any acids or bases to piranha or spraying it with water will accelerate the reaction potentially causing an explosion. This includes photoresist, which is a strong base.

Mixing hot piranha with organic compounds may cause an explosion. This includes acetone, photoresist, isopropyl alcohol, and nylon.

Are you seeing a common thread here? Explosion.

Piranha solutions are extremely energetic and may result in explosion or skin burns if not handled with extreme caution.

Alternatives?
Hexavalent chromium is extremely toxic and piranha solution is very reactive, so why use them?

Adequate cleaning of most glassware for tissue culture purposes can be achieved by washing in hot water (70°C+) with commercial detergents, rinsing with hot tap water (70° C+), and finally rinsing with distilled and double-distilled water.

However, highly contaminated glassware can be cleaned by some other proven method such as (1) ultrasonic cleaning, (2) washing with sodium pyrophosphate, or (3) boiling in meta-phosphate (Alconox), rinsing then boiling in a very dilute .15% hydrochloric acid solution, and then finally re-rinsing.

As a last resort consider using a 95% Ethanol/Hydrochloric Acid bath or 95% Ethanol/Potassium Hydroxide bath as an alternative. These methods can be used effectively against organic residues (caution: this procedure may etch glassware). Several other methods of varying degrees of complexity are also available, along with Nochromix, a commercial formulation that contains ammonium persulfate. It is a powder that is mixed with water and added to 98 percent sulfuric acid, forming a clear solution. In fact, spent solutions of Nochromix can be safely disposed of (after elementary neutralization) via the sanitary sewer if not contaminated with other metals or toxic substances. PCC-54 is good for cleaning pipettes and other lab equipment with hard-to-clean crevices and decontamination.

There are fewer alternatives to piranha solution for the microfabrications labs. However rather than mixing up large volumes of piranha, it may be directly applied to the material, applying the sulfuric acid first, followed by the peroxide.

A second type of piranha etch is the base piranha: a 3:1 mixture of ammonium hydroxide (NH_4OH) with hydrogen peroxide (H_2O_2). This mixture a slightly safer alternative since is not self-starting and must be heated to 60 degrees centigrade before the reaction begins.

In conclusion there are alternative to these dangerous cleaning methods. A final alternative is, if the glassware is that dirty, why not just replace the glassware?

At what point do you decide to throw it out?

Paws for Safety

The "Paws for Safety" program was held in February intended as an outreach to the Tufts University student community with the goal of preventing injury and property damage from fire, smoke and water from sprinkler activation by raising awareness.

The 3 days of the Tufts Paws for Safety event involved 21 trained therapy dogs (many different breeds –from Chihuahua to St. Bernard!) and their 19 handlers- all volunteers. Thank you.

The 2 day event was organized jointly between the Tufts University public safety / EHS organizations and the Tufts community (students, faculty, and staff) – with the Therapy Dogs as the common attraction that attracted the attention of busy people. The dogs were the real stars of the show… and the primary source of warmth and smiling faces!

Tufts Fire Safety Office staff were able to interact with approximately 500 individuals and distributed small rulers imprinted with Fire Safety Office website and telephone contact information.

We plan to make this an annual event. We may organize the event in early December next year and address the fire hazards associated with the holiday season- candles, dry evergreens and hanging electrical lights- all festive but potentially harmful.

For more information on this and other programs, please visit the Fire Safety website at http://publicsafety.tufts.edu/firesafety/