Laboratory Glassware Cleaning

Laboratory glassware is valued for its durability, inertness, transparency and for presenting a simple, clean surface for a variety of applications. It is important that lab glassware is appropriately cleaned as residual contaminants can affect experimental results. Solid deposits on glassware can be the most difficult to remove. Small ions such as chloride ions can diffuse into a few layers of silica over time. Some ions, such as phosphates, can become strongly adhered to the surface and are tedious to remove completely. Examples of solid deposits on glass can give insight into why glass can be so hard to clean. Calcium carbonate, “lime scale”, is ionically bonded and water insoluble. Solid organic materials are Van der Waals bonded to glass but as strongly as the material’s internal bonding. “Mirrors” of metals like mercury, silver or gallium are a different bonding but very strong as well.

The type of bond created between the glass and its contaminant will determine the adherence strength to the glass surface. Without a good solvent or surfactant for the material to be dissolved in, stronger methods are needed.

Safety Precautions

When cleaning glassware, full shielding of the eyes is a minimum requirement. Even soap solutions can cause eye irritation. Many of the chemicals used in cleaning can easily penetrate the skin, especially when combining them with organic solvents. This is especially true when using some of the stronger chemicals listed later in this document. An example of this is a base bath (alkali in an organic solvent) where the alcohol makes the caustic entry into skin even easier and allows for deeper penetration than aqueous solution alone. Hydrofluoric acid, even in low concentration, will penetrate skin and do great damage to the cells. Sulfuric acid at above 70% is especially damaging, becoming immediately warm and later painful. Concentrated sulfuric with added oxidizers is even worse. In using cleaning agents plan ahead and be deliberate in what you do. In all cases, having immediate access to running water is imperative but full skin protection is the first choice. Chemical Splash goggles, plastic aprons and non-disposable gloves – specifically chosen to handle extended contact with the chemical - should be worn during any of the aggressive procedures described below.

Initial Glass Cleaning

When cleaning lab glassware the following procedures should be followed. If the glassware isn’t clean after these initial steps you can go on to more aggressive cleaning protocols.

- Scrape away any thick solid material from the glass if possible. Wipe away any grease from the glass joints with a solvent like acetone which can be used to help remove the grease.
- Put the glassware in a warm cleaning solution of detergent and water.
- Use a brush or cleaning pad to clean any residue or contamination.
- Rinse with tap water first, followed by deionized water and allow to dry.

If your glassware calls for further cleaning action, start with gentle solvents before moving on to more aggressive methods. After using the cleaning methods below a final washing using the initial cleaning mentioned above should be followed as the last step in cleaning.

Mild Cleaning Methods

For thick, brittle deposits on glass simple scraping with something that won't scratch the glass is the best first step (see above). However, this will not remove all the deposits and soft deposits such as grease, or adhering polymers won't yield to scrubbing very well. Additionally, there are parts of glassware where brushes and cloths simply cannot reach. Your next step is to try gentle solvents for long term soaking. When dealing with the gentle aqueous solutions described below this can be enhanced by either heat soaking or, in some instances, mechanical agitation such as stirring, shaking, or sonication.

Common Gentle Aqueous Cleaning Mixtures

Mixture	*Uses*
Deionized water	For diluting out absorbed ions – passive soaking.
Dilute surfactants	Solubilizing lipid material – agitation, brushing, rubbing or sonication.
Protein or saccharide hydrolyzing enzymes	Breaking larger structures into soluble molecules – passive soaking.
Metal chelating compounds	Insoluble salts become more so by removing the metal ion – passive soaking.
Dilute strong acids	Insoluble salt's anion is soluble as its acid form – soak or agitation.
Concentrated weak acids	Insoluble salt's anion is soluble as its acid form – soak, sonicate or brush.
Dilute solutions of: Phosphates, Carbonates or Ammonia	All create low levels of hydroxide ions for solubilizing weak insoluble acidic solids or hydrolyzing ester bonds – soak, agitate or sonicate.

Using Organic Solvents

Organic solvents are often used to remove contaminants from glass. Basically, if it can be readily dissolved in an organic solvent it can be removed by these means. The use of organic solvents is complicated due to their flammability and toxicity. When working with solvents proper ventilation and appropriate PPE (suitable glove compatibility with the solvent) are necessary. Solvent baths should be contained and the area of open solvent should be minimized in order to limit evaporation. Moistening a cloth with solvent is good for easily accessed surfaces. Agitating solvent inside of a glass container is another method.

Aggressive Cleaning Methods

Being unable to remove the adhered material with the above relatively gentle and safe solvents, stronger chemical persuasion is warranted. With as much residue removed as otherwise possible, the next actions are to either release the adhered material by removing the top layer of silicon oxide or to oxidize the material itself from the glass surface.

Removing Underlying Silicon Oxide Layer

Laboratory "glass" is a polysilicate solid, though it can include many other oxides in lesser amounts for specialized uses (boron is included in the commonly used Pyrex®) and sodium or potassium ions are generally present. The surface is bounded with hydroxyl and oxide attached to silicon. Sometimes surface functional groups on the glass will bind to the contaminant. One way to remove these contaminants is to literally remove the outer layer of glass. To do this the silica layer must be cleaved. This can be accomplished by using dilute hydrofluoric acid or a base bath (sodium or potassium hydroxide in either ethanol or isopropanol). Your glassware should be soaked in the solution for a sufficient period before being rinsed and cleaned with your usual detergent. The hydrofluoric acid solution should be about 2% and used for a brief period so as to not etch the glass more. Hydrofluoric acid is not commonly used for glassware cleaning but it does have some special applications such as cleaning clogged glass frit filters.

Oxidizing Contaminants from Glassware

Often the residue on glass is insoluble to organic solvents, surfactant solutions, or mildly acidic solutions. At this point one of the common ways to clean glass is to oxidize the contaminant in order to render it soluble. Having as little depth as possible to act on a residue is an advantage for both thoroughness and minimizing the amount of an energetic reaction and gas that may be produced by the reaction. There are several common formulas that can be used in order to oxidize contaminants from the glass surface.

Aqua regia, consists of a 1:3 ratio of nitric and hydrochloric acid. It is an aqueous based acidic oxidizing solution and is similar to hydrochloric acid but has the added excitement of an acid-boosted nitric oxidizer.

A number of solutions using **sulfuric acid** can be used and will be discussed with more detail below. In these solutions the sulfuric acid is usually close to 100 to start with but becomes diluted quickly as it acquires water from the air and from contaminants. Other formulations use very concentrated but aqueous sulfuric acid, at 50% or 70%. The amount of oxidizing additives to be added to sulfuric acid can widely vary; sometimes a certain minimum amount is added for effective cleaning and more is added when the potency seems to diminish.

- One of the most common sulfuric acid-based cleaners is a “chromic acid solution”. This can be prepared by adding solid chromium (VI) oxide, potassium dichromate or potassium chromate – in widely varying amounts – to sulfuric acid. The well-known Chromerge® is a commercially-available material for generating a chromic acid solution. NOCHROMIX®, which contains ammonium peroxydisulfate as the main ingredient, is a common alternative to chromic acid. This is metal-free and non-carcinogenic and the lack of chromium makes disposal easier.
- **Piranha solution** is hydrogen peroxide in near fully concentrated sulfuric and can be purchased as is, pre-mixed. Hydrogen peroxide is most stable in acid but will slowly decompose to oxygen and water, requiring a vented cap (which “spits” sulfuric acid when the containers are in transport)
- **Fuming sulfuric acid** has added sulfur trioxide, 10-20%, which makes pyrosulfuric acid – an even more potent hydrogen ion. Pyrosulfuric acid can oxidize organic material more than concentrated sulfuric acid can.

TIP: Knowing when potency is effectively lost is a time-saver in operations requiring fast turn-around of glassware. Below are a few tips on how to identify the concentration of your cleaner.

- Chromate based cleaners have the built-in color indicators making it easy to identify the ratio of chromate (orange) to chromium III (blue-green).
- The viscosity of sulfuric acid will be reduced as water, absorbed air humidity, gets added to the cleaner.
- Alcoholic base baths may become even more colored and will certainly absorb carbon dioxide from the room air to neutralize potent hydroxide or alkoxide ions.

Neutralization and Disposal

Neutralization of these aggressive baths is not a trivial matter, largely due to the volume of the baths commonly employed. The UW-Madison Laboratory Safety Guide provides descriptions of neutralization procedures (see Chapter 7 starting on page 164). Extreme care must be taken and appropriate PPE must be worn. No one should do these neutralizations without the proper training. The Chemical Safety Office staff can help you with the process by reviewing your procedures. In general, the neutralization process will render these safe to go down the drain – *assuming you have followed the correct procedure!* Contact us at chemsafety@fpm.wisc.edu for questions and advice.

Sources:
Personal experience and observations of John Straughn
Chemist's Companion, Gordon and Ford, Wiley 1969
Suggestions for Cleaning Glassware, Corning, 2009

March 2013

For More Information Contact:

Environment, Health and Safety Department
30 East Campus Mall, Madison, WI 53715-1227
Phone (608) 265-5000 · **Fax** (608) 262-6767;
The Chemical Safety Office