Bartlett Group

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Standard Operating Procedures

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USE OF THE BASE and ACID BATHS, GENERAL HANDLING OF ACIDS AND BASES

Minimum PPE:

1. Safety glasses, the Big Rubber ones that completely shield the eyes from splashing
2. Neoprene Gloves, long black gloves
3. Lab Coat

Warning:

The solution in the base bath is extremely corrosive and can cause serious burns. Therefore, neoprene gloves with long cuffs ("opera gloves") must be worn, as latex gloves will not provide adequate protection to the hands.

Procedure for Base Bath:

I. Pre-washing soiled glassware.

1. All soiled glassware should be prewashed with appropriate solvents to get the glassware as clean as possible, being sure to collect the solvents in a container, then put the used solvent into the appropriate waste container.

2. Wash the glassware with detergent and rinse with distilled water.

II. Preparation of Base Bath

1. Dissolve 200-300 g of KOH into 1 L H_2O
2. Slowly add that solution to 8 L of Isopropanol

III. Using the base bath.

1. Before working with the base bath, be sure that your gloves are in good condition. Replace them if you have any doubt as to their condition.

2. While wearing the big rubber safety goggles and neoprene gloves, glassware that has been prewashed according to the above procedure is gently lowered into the base bath

allowing the solution to completely fill the glassware. Be careful to avoid splashing base bath solution onto yourself as air is displaced from your glassware.

3. Allow the glassware to remain in the solution several hours or overnight.

4. While wearing safety goggles and neoprene gloves, remove glassware from the base bath allowing as much of the solution to drain as is possible.

5. Rinse the alcoholic solution from the glass with tap water. Make sure to first turn on the water, and then place the glassware under the stream making sure not to splash any on you

6. Rinse with distilled water.

7. Rinse with acetone and place on the drying rack.

8. After 15 min. the glassware may be placed in a drying oven.

Cautions:

1. Glassware can be etched from prolonged exposure to the basic solution. Quartz glassware is too expensive to routinely expose to this risk. It should not be cleaned with a base bath
2. Do NOT put any of the following items into the KOH/EtOH bath:
   - volumetric glassware
   - stopcock keys
   - glass frits/filters
   - rubber items
   - IR or UV cells or NMR tubes
   - fragile or broken glassware
   - glassware that still has grease or bulk dirt on it
   - anything with mercury, sodium, potassium metal

3. The base bath should be stored in secondary container to eliminate spills and covered at all times.

VI. Maintenance

1. Base baths should be disposed of properly and replaced with new base/alcohol solutions as the cleaning ability decreases. Normally the base bath is useable for several months. If the base bath has turned orange, it should be replaced.

2. To deactivate the base bath: Add dilute HCl very slowly to the base bath to neutralize it. Check the pH frequently with pH paper. After neutralization, pour the mixture down the drain (if it contains less than 24% alcohol) or package as hazardous waste for disposal (if it contains more than 24% alcohol).

Procedure for Acid Bath:

NB: As of Fall 2016, the lab is no longer maintaining an acid bath.

I. Pre-washing soiled glassware.

1. All soiled glassware should be prewashed with appropriate solvents to get the glassware as clean as possible, being sure to collect the solvents in a container, then put the used solvent into the appropriate waste container.

2. Wash the glassware with detergent and by rinse with distilled water.

II. Preparation of Acid Bath

1. Wearing a lab coat, safety goggles, and acid resistant gloves carefully add 100 mL of 12M HCl to 900 mL of DI H_2O to make 1 liter of acid bath. *REMEMBER, **A**DD **A**CID TO THE WATER.* An acid bath is prepared in the large waste buckets found in the hallways. Prepare enough solution to completely submerge the glassware.

III. Using the acid bath.

1. Before working with the acid bath, be sure that your gloves are in good condition. Replace them if you have any doubt as to their condition.

2. While wearing the big rubber safety goggles and neoprene gloves, glassware that has been prewashed according to the above procedure is gently lowered into the base bath *allowing the solution to completely fill the glassware.*

3. Allow the glassware to remain in the solution several hours or overnight.

4. While wearing safety goggles and neoprene gloves, remove glassware from the acid bath allowing as much of the solution to drain as is possible.

5. Thoroughly rinse the solution from the glass with tap water. Make sure to first turn on the water, and then place the glassware under the stream making sure not to splash any on you

6. Rinse with distilled water.

7. Rinse with acetone and place on the drying rack.

8. After 15 min. the glassware may be placed in a drying oven.

Cautions:

Do not place rubber in the acid bath

Process: USE OF THE BASE and ACID BATHS, GENERAL HANDLING OF ACIDS AND BASES

Locations of Acids and Bases:

Acids are found in Rm 2624 in the metal cabinet near ground level, except for nitric acid, which is found in the small wooden cabinet across from the aqua regia hood in Rm 2624.

Bases are found in Rm 2616 in the bottom right cabinet of the hood near the rotovap. .

Handling Acids and Bases:

Goggles and safety glasses must be worn when handling any chemical in the lab. To carry 4 L bottles, a secondary container must be used. These are found near the door entrances in Rm's 2624 and 2616. Be aware of any special hazards that accompany the particular acid or base you are using and any incompatibilities that exist between the acid/base and chemicals you are working with. ***Violent and very dangerous reactions can occur***, especially when working with concentrated stock reagents!

Author and Date: Yenting Kuo January 16, 2012
Last Revised: Daniel A. McCurry February 2, 2017
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WORKING WITH STRONG OXIDANTS

Oxidizing chemicals are materials that spontaneously evolve oxygen at room temperature or with slight heating or promote combustion. This class of chemicals includes peroxides, chlorates, perchlorates, nitrates, and permanganates. Strong oxidizers are capable of forming explosive mixtures when mixed with combustible, organic or easily oxidized materials. Examples of strong oxidizers are listed at the end of this SOP.

Engineering Controls

Work with strong oxidizing agents should be conducted in a fume hood. Sash height should be kept low to avoid release of fumes and provide a physical barrier.

Work Practice Controls

1. Minimize the quantities of oxidizers on hand.
2. Exercise caution when mixing oxidizing agents with flammable or combustible materials for research. Use small amounts to reduce generation of heat and control the reaction.
3. Evacuated glassware can implode and eject flying glass, and splattered chemicals. Vacuum work involving oxidizing chemicals must be conducted in a fume hood, glove box, or isolated in an acceptable manner.
4. Mechanical vacuum pumps must be protected using cold traps and, where appropriate, filtered to prevent particulate release. The exhaust for the pumps must be vented into an exhaust hood.

Decontamination procedures

Personnel: Wash hands and arms with soap and water immediately after handling oxidizing chemicals.

Area: Carefully clean work area after use. Paper towels or similar materials contaminated with strong oxidizing chemicals may pose a fire risk.

Emergency procedure

Report all emergencies, suspicious activity, injuries, spills, and fires to the University of Michigan Division of Public Safety and Security (DPSS) by calling 911 or texting 377911.

Exposures/Unintended Contact: If in need of emergency chemical attention, call 911 immediately. Flush exposed eyes or skin with water for at least 15 minutes. Check SDS for chemical-specific exposure treatment and first-aid activities.

Contact OSEH for advice on symptoms of chemical exposure, or assistance in performing an exposure assessment.

Report all work related accidents, injuries, illnesses or exposures to Work Connections within 24 hours by completing and submitting the Illness and Injury Report Form. Follow the directions on the Work Connections website Forms Instructions to obtain proper medical treatment and follow-up.

Complete the OSEH Laboratory Incident and Near-Miss Report form.

TREATMENT FACILITIES:

U-M Occupational Health Services -- *Campus Employees*
Mon-Fri 7:30 am - 4:30 pm
After hours - go to UM Hospital Emergency Dept. – Urgent Care Clinic
C380 Med Inn building
1500 East Medical Center Drive, Ann Arbor (734) 764-8021

University Health Services -- *University students (non-life threatening conditions)*
Mon-Fri 8 am – 4:30 pm, Sat 9 am – 12 pm
Contact for current hours as they may vary
207 Fletcher Street, Ann Arbor (734) 764-8320

UMHS Emergency Department -- *after clinic hours or on weekends*
1500 East Medical Center Drive, Ann Arbor, (734) 936-6666

Eye protection

Eye protection in the form of safety glasses must be worn at all times when handling oxidizing chemicals. Ordinary (street) prescription glasses do not provide adequate protection. (Contrary to popular opinion these glasses cannot pass the rigorous test for industrial safety glasses.) Adequate safety glasses must meet the requirements of the Practice for Occupational and Educational Eye and Face Protection (ANSI Z.87. 1 1989) and must be equipped with side shields. Safety glasses with side shields do not provide adequate protection from splashes; therefore, when the potential for splash hazard exists other eye protection and/or face protection must be worn.

Eyewash

Where the eyes or body of any person may be exposed to oxidizing chemicals, suitable facilities for quick drenching or flushing of the eyes and body shall be provided within the work area for immediate emergency use. Bottle type eyewash stations are not acceptable.

Gloves

Gloves should be worn when handling oxidizing chemicals. Disposable nitrile gloves provide adequate protection against accidental hand contact with small quantities of most laboratory

chemicals. Lab workers should contact EHRS for advice on chemical resistant glove selection when direct or prolonged contact with hazardous chemicals is anticipated.

Hazard assessment

Hazard assessment should address proper use and handling techniques, fire safety, storage, and waste disposal issues.

Protective apparel

Lab coats, closed toed shoes and long sleeved clothing should be worn when handling oxidizing chemicals. Additional protective clothing should be worn if the possibility of skin contact is likely.

Safety shielding

Safety shielding is required any time there is a risk of explosion, splash hazard or a highly exothermic reaction. All manipulations of oxidizing chemicals which pose this risk should occur in a fume hood with the sash in the lowest feasible position. Portable shields, which provide protection to all laboratory occupants are acceptable.

Safety shower

A safety or drench shower should be available in a nearby location where the oxidizing chemicals are used.

Signs and labels

Containers: All oxidizing chemicals must be clearly labeled with the correct chemical name. Handwritten labels are acceptable; chemical formulas and structural formulas are not acceptable.

Special storage

Oxidizers should be stored in a cool and dry location away from flammable and combustible materials. Keep oxidizers segregated from all other chemicals in the laboratory. Minimize the quantities of strong oxidizers stored in the laboratory.

Do not store on wooden shelves or in wooden cabinets.

Do not use corks or rubber stoppers.

Never return excess chemicals to the original container. Small amounts of impurities may be introduced into the container which may cause a fire or explosion.

Special ventilation

All halogens and other volatile oxidants must be handled in a laboratory fume hood.

Spill response

Anticipate spills by having the appropriate clean up equipment on hand. The appropriate clean up supplies can be determined by consulting the material safety data sheet. This should occur prior to the use of any oxidizing chemicals. Spill control materials for oxidizers are designed to be inert and will not react with the reagent. Never use paper towels or other inappropriate materials which are combustible. The waste materials generated during spill cleanup may pose a flammability risk and should not remain in the laboratory overnight unless it is stored in an appropriate container.

In the event of a spill. Alert personnel in the area that a spill has occurred. Do not attempt to handle a large spill of oxidizing chemicals. Vacate the laboratory immediately and call for assistance. Remain on the scene, but at a safe distance, to receive and direct safety personnel when they arrive.

Vacuum protection

Evacuated glassware can implode and eject flying glass, and splattered chemicals. Vacuum work involving oxidizing chemicals must be conducted in a fume hood, glove box or isolated in an acceptable manner.

Mechanical vacuum pumps must be protected using cold traps and, where appropriate, filtered to prevent particulate release. The exhaust for the pumps must be vented into an exhaust hood.

Waste disposal

All materials contaminated with oxidizing chemicals pose a fire hazard and should be disposed of as hazardous waste. Alert the Office of Environmental Health and Radiation Safety if you generate wastes contaminated by oxidizers. Do not let contaminated wastes remain in the laboratory overnight unless proper containers are provided.

Examples of Strong Oxidizers

Ammonium perchlorate	Ammonium permanganate
Barium peroxide	Bromine
Calcium chlorate	Calcium hypochlorite
Chlorine trifluoride	Chromium anhydride
Chromic acid	Dibenzoyl peroxide
Fluorine	Hydrogen peroxide
Magnesium peroxide	Nitrogen trioxide
Perchloric acid	Potassium bromate
Potassium chlorate	Potassium peroxide
Propyl nitrate	Sodium chlorate
Sodium chlorite	Sodium perchlorate
Sodium peroxide	

Source: CRC Handbook of Laboratory Safety, 3rd edition.

This was adapted, after review by BTK, from the University of Pennsylvania. http://www.ehrs.upenn.edu/programs/labsafety/chp/sop/oxidizers.html accessed 2 Oct 2009

2017 Revisions adapted from the University of Michigan. http://ehs.umich.edu/wp-content/uploads/sites/37/2016/02/OxidizingChemicals.docx accessed 2 Feb 2017

Author and Date: Bruce Kraay March 6, 2013
Last Revised: Jimmy Brancho February 13, 2017
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WORKING WITH AQUA REGIA

Introduction

Aqua regia is a corrosive, fuming yellow liquid prepared by slow mixing of one volume of concentrated nitric acid with three volumes of concentrated hydrochloric acid. It is used to dissolve metals such as gold, platinum, silver, etc. Its fumes and yellow color are caused by reaction of nitric acid, HNO_3, with hydrogen chloride, HCl, to form nitrosyl chloride (NOCl), chlorine (Cl_2), and water; both chlorine and nitrosyl chloride are yellow-colored and volatile. It is commonly used as a cleaning agent, and due to its highly corrosive nature, should be handled with extreme caution.

Personal Protection Equipment

When working with aqua regia, all work should be done inside the acid fume hood. Goggles, gloves and a lab apron should be worn at all times while handling aqua regia.

Preparation

Add 1 part HNO_3 to 3 parts HCl with slow pouring inside of the acid fume hood. The appearance of an orange/red solution color and gas bubbles is an indication that the reaction is progressing.

Handling

The acid fume hood should only be used for aqua regia cleaning. Glassware should be cleaned with soap and water to remove residual organics prior to cleaning with aqua regia. Never bring any organic chemicals into the hood and never remove aqua regia from the fume hood. Do not bring any metal stopcock holders, spatulas, etc. to the acid hood. Only prepare the amount of aqua regia necessary to clean the glassware of interest, as the reaction proceeds upon mixing and extra aqua regia both increases the safety concern and increases the amount of wasted reagents. When working with aqua regia in the hood, the extent of reaction can be observed visually by the production of gas which can be liberated by tapping on the side of the container. Under no circumstances should aqua regia be placed in a closed container. The gases generated will build up pressure which will create a hazardous situation. When you are not actively using aqua regia, always ensure that the fume hood sash remain down and closed.

First Aid

If an individual is harmfully exposed to aqua regia the following measures summarized below can be taken. For serious injuries, 911 should be called and immediate medical attention should be sought.

Inhalation **-** Move the exposed person to fresh air at once. Perform artificial respiration if breathing has stopped. Keep the affected person warm and at rest. Get prompt medical attention. When unconscious, loosen tight clothing and position in
secured recovery position.

Ingestion **-** NEVER MAKE AN UNCONSCIOUS PERSON VOMIT OR DRINK FLUIDS! Promptly get affected personnel to drink large volumes of water to dilute the swallowed chemical. DO NOT induce vomiting. Get medical attention immediately.

Skin **-** Wash off promptly and flush contaminated skin with water. Promptly remove clothing if soaked through and flush skin with water. Get medical attention if irritation persists after washing.

*Eyes***-** Promptly wash eyes with plenty of water while lifting the eye lids. Continue to rinse for at least 15 minutes and get medical attention.

Spill/Accident

The level of response for an aqua regia spill depends on the amount of spill, completion of the reaction and the location of the spill. If a volume exceeding 200 mL is spilled at anytime, 911 should be called to activate the spill response team. For spills less than 200 mL in the hood with the reaction is complete (no bubbles in solution), the acid can be neutralized using an acid spill kit, found on the front shelving unit on the lower left side, followed by the use of adsorbent pig mat to soak up the spill. If the reaction has not yet completed, close the hood sash and wait for reaction completion before cleaning up the spill as described above. If aqua regia of any volume is spilled outside of the acid fume hood, evacuate the lab and call 911 to activate the spill response team.

Disposal

When disposing aqua regia, place the solution in the properly labeled glass waste containers (located inside of the acid fume hood). The waste containers should never be filled more than halfway and the cap should never to completely tightened. Ensure that nothing but aqua regia is placed in the waste containers as aqua regia is a strong oxidizing agent and will react with organic chemicals. When the container is half full, lightly cap and submit to OESO for disposal.

*Adapted for use from www.cchem.berkeley.edu/rsgrp/**SOP**s/**Aqua Regia**.doc and the Duke University Aqua Regia SOP.*

Author and Date: Charles Lhermitte — April 11, 2014
Last Revised: Sam Esarey — February 3, 2017
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WORKING WITH PIRANHA CLEANING SOLUTION

General:

1. Piranha is used to remove organic residues from substrates. Two different solutions are used. The most common is the acid piranha: a 3:1 mixture of concentrated sulfuric acid (H_2SO_4) with hydrogen peroxide (H_2O_2). Also used is the base piranha: a 3:1 mixture of ammonium hydroxide (NH_4OH) with hydrogen peroxide (H_2O_2). Piranha acid can reach temperatures in excess of 100 °C upon addition of hydrogen peroxide (always add H_2O_2 *to* H_2SO_4, not vice versa). Piranha base requires heating the solution to 60 °C before the solution is “activated”. In both instance be extremely careful with hot piranha.
2. There are many things which will cause the reaction to accelerate out of control. The reaction is "out of control" anytime the solution is not contained in the preparation vessel i.e. foaming out of the container to the bench-top or floor, to an explosion with a huge shock wave including glove and acid-gown shredding glass sharps. Piranha burn organic compounds. If you provide sufficient fuel for it (i.e. organics or solvents such as isopropanol or acetone), it will generate enormous quantities of heat and gas **(VERY DANGEROUS).**
3. No undergraduates or rotation students may make or use Piranha solutions. Only permanent Bartlett lab members are authorized to make and use piranha solution. If you must make Piranha solution, you must ask a Bartlett group member (graduate student or post-doc) to assist you.

Protective Equipment:

1. The handling of Piranha solutions requires special protection equipment in addition to the regular personal protective equipment (PPE).
2. The additional protective equipment includes: full goggles, heavy duty rubber gloves (regular Nitrile gloves will **not** provide sufficient protection), as well as an acid apron to wear *on top* of the lab coat.

Piranha Solution Handling:

1. Piranha solutions, as well as any corrosive or hazardous substances, can only be used in lab if there is another lab member present and aware of its use.
2. Whenever handling Piranha, only use glass containers (preferably Pyrex). Containers used during the experiment must be clearly labeled, and a warning sign, visible by any user working under the flow hood, must be posted at all times to indicate that the solutions contain Piranha mixture. Secondary glass or Teflon containers should also be used to contain small spills.
3. Mix the solution in a fume hood with the sash between you and the solution. Wear the full protection. MAKE SURE THERE ARE NO ORGANICS NEARBY! PIRHANA MAY

NOT BE USED IN A HOOD THAT ALSO CONTAINS ORGANIC MATERIALS. THE TWO MUST BE SEPARATED FROM ONE ANOTHER.

4. When preparing the piranha solution, always add the peroxide to the acid. The H_2O_2 is added immediately before the etching process because it immediately produces an exothermic reaction with gas (pressure) release. If the H_2O_2 concentration is at 50% or greater, an explosion could occur (only make solutions that are 1:3 H_2O_2:H_2SO_4 or 1:3 H_2O_2:NH_4OH). Warm Piranha should be used for most effective reactivity, so it should be made immediately before its intended use.
5. Piranha solution is very energetic and potentially explosive. It is very likely to become hot, more than 100°C. Handle with care to prevent burns.
6. Substrate should be rinsed with ***water*** and dried before placing it in a Piranha bath. The substrate *should not* be rinsed or dried with acetone (since Piranha reacts violently with organics) immediately before placing it in a Piranha bath. Water should always be the last rinse for the substrate before placing it in the warm Piranha bath.
7. After cleaning, carefully remove the substrate from the bath, and wash with water (into waste jar) to remove and dilute additional acid.
8. Leave the remaining hot piranha solution in an open container until cool, then transfer to a waste container specialized to handle Piranha solution (with vented cap)
9. Never store hot piranha solutions. Piranha stored in a closed container will likely explode.
10. Adding any acids or bases to Piranha or diluting with water will accelerate the reaction.
11. Mixing hot piranha with organic compounds may cause an explosion. This includes acetone, isopropyl alcohol, and nylon.
12. Do not store wash bottles containing organic compounds near Piranha solutions.

Piranha Waste Disposal:

1. The primary hazard from storage of piranha waste is the potential for gas generation and over-pressurization of the container when the solution is still hot. If you store a hot solution in an air tight container, it will explode!
2. Therefore prior to storing the piranha solution, it must be left in an open container in order to cool down for several hours (overnight). Make certain that the open container is clearly labeled and left in a safe area for overnight cool down.
3. Once cooled down, the solution can be transferred into a closed glass container (see next point) for waste storage. The container must be very clearly labeled with the solution name and composition and must include VERY VISIBLE warning signs not to add any other types of chemicals.
4. Piranha waste MAY NOT be stored in regular waste containers. You MUST use a special waste bottle that has a vented cap. If you store Piranha wastes in a regular waste container it may explode if pressure build inside it too rapidly. This is why we need the special waste containers. These waste bottles may be obtained from Laurie MacDonald. Just let her know that you need a waste bottle for Piranha and she will give you one.

Emergency Procedure:

1. In case of large exposure, the victim should be removed from the contaminated area, and placed under a safety shower while emergency personal is contacted (911).
2. All contaminated clothing should be removed immediately with appropriate gloves and safely discarded.
3. In case of contact with the skin, the affected area must be immediately rinsed with large amounts of water for at least 15 min.
4. In case of contact with the eye, irrigate the eye for at least 30 minutes, keeping the eyelids apart and away from eyeballs during irrigation. Place ice pack on eyes until reaching emergency room.
5. In case of inhalation, it 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.

Supply and Storage of Piranha Solutions:

Do not store Piranha. Mix fresh solution for each use. Excess solutions should be disposed as explained in paragraph #4.

Author and Date: James Brancho January 19, 2012
Last Revised: Adam Crowe February 2, 2017
Reviewed and Approved: Bart M. Bartlett February 3, 2017

USING THE SCHLENK LINE

I. Overview

The Schlenk line is an extremely useful system for many chemists, allowing the conduction of air- and/or water-sensitive reactions without the expense and restriction of a glove box. The Schlenk line can be configured to pipe in any gas, but argon and nitrogen are most commonly used to provide an inert atmosphere for sensitive reactions. When used correctly, the Schlenk line is an invaluable asset; however, correct use is complicated and involves many extra steps. Additionally, there are several serious hazards that can present themselves with inappropriate use. The new user must be acquainted with the following procedures if he is to successfully utilize the line without damage to himself or others.

II. Common Materials

The Schlenk Line: The lines in the Bartlett group laboratory consist of two separate glass tubes. The top tube is the *vacuum line*, and the bottom tube is the *nitrogen line*.

The Nitrogen Line: The nitrogen line begins in the wall of the hood with the common nitrogen source. The hose exits the wall and forces nitrogen through a dessicating column filled with Drierite. This removes any water vapors present in the nitrogen stream. If your Drierite is pink, change the column before continuing use, as it is no longer effectively drying your stream. Unused Drierite is blue in color.

The nitrogen is then fed into the Schlenk line, where it can be directed into glassware by opening the ports on the line (partially unscrewing the bottom stopper). The nitrogen line continues to a mineral oil bubbler, which serves as a gas barrier between the nitrogen line and the ambient oxygen-containing atmosphere of the hood. The bubbler is also an indicator to the user that a pressure equilibrium is established in the line. This is discussed in Section III, but for

now: when your nitrogen flow is running, if you do not see bubbles coming out of the mineral oil bubbler, you are building up pressure in the line and headed for an explosion. Gas flow into the bubbler can be adjusted by the valves at various points throughout the line.

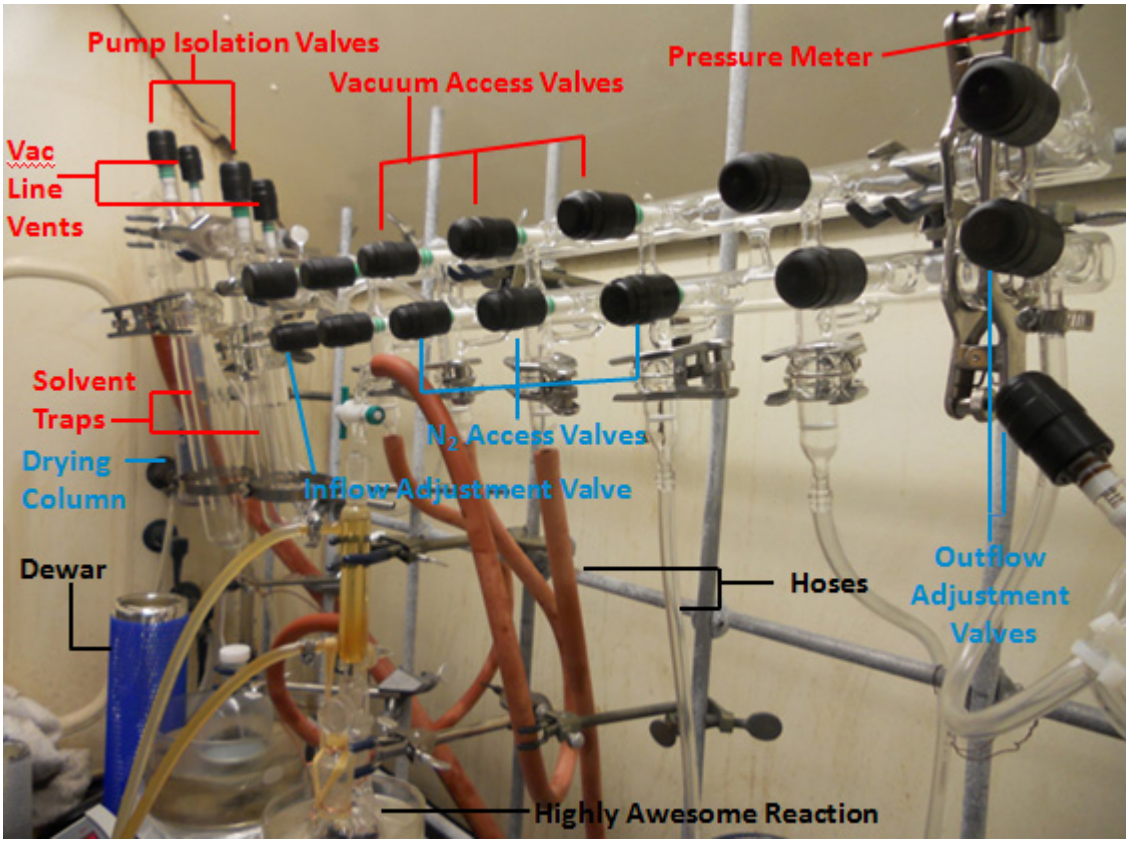


Figure 1: A diagram of all of the important Schlenk line components. The mineral oil bubbler is off-camera to the right.

The Vacuum Line: The vacuum line begins beneath the hood at the vacuum pump. The pump removes gases from the vacuum line, pulling them down into the pump and then exhausting them. The pump can be isolated from the vacuum line by means of the first big valve where the vacuum pump hose meets the line. Immediately after the pump isolation valve is the main vent for the line. The vacuum line can be vented (returned to ambient pressure) by the slow opening of this valve. Beneath these two valves is a glass cylinder called a solvent trap, discussed further in section IV. There is another set of pump isolation and venting valves, along with another trap, immediately after the first trap.

Similar to the nitrogen line, the vacuum line continues past several ports that can be opened to expose glassware to vacuum. The vacuum line culminates in a pressure meter that measures the pressure inside the vacuum line. This number is critical and should be monitored while the vacuum is running.

Hoses: Made of tough, stretchy materials such as rubber or Nalgene, hoses form an airtight seal between the Schlenk line and any connected reaction flasks. These should always be checked for appropriate fit and for gashes or holes.

Vacuum Grease: The vacuum grease in use in the Bartlett lab contains siloxanes and silica. It is used to seal any joints in the glassware setup to improve the gas barrier between the flask and the ambient environment. Do not grease any portion of the Schlenk line itself, it has been designed to keep an air tight seal without the use of grease and the application of grease can reduce its effectivness.

Schlenk Glassware: Schlenk glassware has been specially made to withstand the temperature and pressure fluctuations associated with Schlenk procedures, specifically to withstand high vacuum without implosion. Glassware should always be inspected for cracks and defects before use. There are many various pieces, such as gas adapters, multi-necked flasks, distillation heads, etc., and the exhaustive list will not be covered here.

Dewars: These dewars are used for holding the liquid nitrogen coolant that will be used to cool the traps during vacuum procedures. Though they may look metal, they are made of a special type of glass and also contain a vacuum chamber, so they will break loudly and violently if dropped. As a result, dewars should be handled with care, and stored in areas away from traffic or ledges.

Liquid Nitrogen: Liquid nitrogen is a cryogenic cooling agent that is used to prevent organic solvents from entering the pump oil. Its temperature is -196 C, so skin contact should be avoided. Burns and blisters may result from contact, though the pain is not more than a slight stinging. Insulated gloves should be used while handling and pouring liquid N_2. NITRILE GLOVES SHOULD **NOT** BE WORN, AND ANY HAIR TIES ETC. SHOULD BE REMOVED FROM WRISTS BEFORE USE. These items will freeze to the skin and prolong the exposure, leading to more serious burns!

III. Safety Concerns

Keeping a Pressure Equilibrium: The nitrogen line is designed, when used properly, to maintain equal pressure between each reaction flask and the inside of the line, and a slight positive pressure compared to the ambient environment (so that oxygen stays out). This is accomplished through the flow adjustment valves at various points throughout the nitrogen line. When you activate the nitrogen flow using the faucet on the hood, check first to make sure that there is gas exiting the mineral oil bubbler. If not, open the flow adjustment valves throughout the line until gas is seen. Without this exhaust, nitrogen pressure builds up in the line and can cause an explosion or ejection of stoppers, septa, etc. from glassware setups. If you close or reduce the output to the mineral oil bubbler, be sure that your system has an alternative exhaust to avoid a dangerous situation! Keep in mind that if you have multiple reactions running on the same Schlenk line the headspace of the flasks will mix. Do not run reactions that are not compatible (i.e. will react) on the same line at the same time.

The Vacuum Pump: The vacuum pump is a powerful machine that is used to create high vacuum within the line. The main safety concern here is periodic maintenance. The pump oil should be changed regularly to mitigate decomposition by organic solvent vapors that may

be pulled into the pump. If the pump ever exhausts thick smoke or a foul odor, or if the pump is performing worse than usual, the pump oil should be changed immediately. The vacuum pump should be capable of pulling a vacuum of about 70-80 mtorr with no cooling traps installed, and at most 30-40 mtorr with traps installed. If you are commonly changing your pump oil due to solvent intake, review the proper procedure for cooling the traps on your line (section IV). If using especially corrosive solvents (acids, thionylchloride, halogens, ect.) consult the vacuum pump manual for setting up the use of the pump gas ballast.

Cracked Glassware: Star cracks and hairline fractures result in glassware from normal handling, especially during cleaning. These easily-overlooked defects weaken the structure of the glass, making it more susceptible to explosions in increased-pressure situations (cannula transfers, refluxes, etc.) and implosions in low-pressure situations (vacuum). Glassware should always be carefully inspected for these defects before use on the line. Broken glassware can be repaired for use later or discarded.

Heating/Freezing Flasks on the Line: All of the same rules apply here as in the Pressure Equilibrium and Cracked Glassware sections. Especially when heating, an exhaust is necessary to ensure that pressure in the flask does not build to intensely high or drop to intensely low levels. Breakage in glassware can be avoided by ensuring that any flask undergoing temperature change is open, either to vacuum or to the nitrogen line as the procedure requires. Heating/freezing a closed system is very rarely necessary and should be done extremely carefully, if at all!

Liquid Nitrogen: Liquid nitrogen is a cryogenic cooling agent that is used to prevent organic solvents from entering the pump oil. Its temperature is -196 °C, so skin contact should be avoided. Burns and blisters may result from contact, though the pain is not more than a slight stinging. Insulated gloves should be used while handling and pouring liquid N_2. NITRILE GLOVES SHOULD **NOT** BE WORN, AND ANY HAIR TIES ETC. SHOULD BE REMOVED FROM WRISTS BEFORE USE. These items will freeze to the skin and prolong the exposure, leading to more serious burns!

Condensing Oxygen: This is the most dangerous hazard associated with Schlenk line use. Liquid oxygen is deposited into your solvent traps when air from the ambient environment is pulled through the vacuum line and then cooled by the liquid nitrogen in the traps. This does not occur during normal use, such as when evacuating a flask containing air, for example. When there is a leak in your vacuum line, or when an active vacuum port has been mistakenly left open to ambient for a period of time, oxygen can be condensed. This is why it is important to watch the pressure meter. If your pressure is suddenly and inexplicably rising, seal off your line ASAP.

Liquid oxygen is extremely reactive and very, very dangerous. The hazard presents itself when the traps are removed and the system begins to heat to room temperature. The oxygen may react explosively with organic solvents that are also in the trap. If that does not happen, then the expansion of the gas due to normal heating can build up pressure within the Schlenk line and cause an explosion in that manner. (Gases take up far more space than liquids do – remember your general chemistry!)

Fortunately, liquid oxygen has a very distinct pale blue color. However, if you are removing your liquid N_2 dewars and you suspect that you have condensed oxygen, replace the dewars immediately, turn off the vacuum, open the system to the atmosphere (with the closest and largest ports available), close the sash, and allow the system to warm slowly as the N_2 in the dewars dissipates.Close the doors on your hood and warn any other labmates present of the explosion hazard. Evacuate the lab and notify Dr. Bartlett. After the traps have come to room temp, consider them still dangerous as peroxides may have formed. Rinse the traps with water into a clean beaker and test the solution with the peroxide strips (located in the 2616 fridge) if peroxides are present, neutralize them with sodium thiosulfate or sodium sulfite before disposing of the waste. O_2 CONDENSATION IS ONLY ACHIEVED THROUGH IMPROPER SCHLENK LINE USE. THINK, AND DOUBLE CHECK, BEFORE DOING ANYTHING ON YOUR LINE.

IV. Setup procedure for Typical Air-Free Work

1) Clean and dry your glassware. Cleaned glassware should be placed in the drying oven for at least 30 minutes before transfer to the Schlenk line. Don't forget a stir bar! The author likes to assemble his entire glassware setup outside the drying oven, then take it apart and put it in. While you're waiting, you could do steps 2-4.
2) Ensure that the main pump isolation valve is shut on your line and that the vent is open, and that all access ports to the vacuum line are closed. Activate the vacuum pump by pressing the switch on the hood. Close all vents to the vacuum line. Open the main pump isolation valve. You should see the value on the pressure meter rapidly decrease. If the meter does not decrease to less than 80 mtorr, turn off the vacuum pump and check the O-rings on your solvent traps and all access ports. If you are sure that your line is not suspect, you may need to change your pump oil.
3) Ensure that flow adjustment valves to the mineral oil bubbler are open, and that all access ports to the nitrogen line are shut. Check the color of your dessicating column. Activate the nitrogen flow and ensure that there is gas exiting the bubbler. If not, ensure that the flow adjustment valves are open.
4) Cool your traps with liquid N_2. The safest way to do this is to fill two appropriately-sized dewars about 1/3 full with liquid N_2. Raise the dewars onto the traps and secure with the clamps. Get a third dewar and fill with liquid N_2. Carefully pour liquid N_2 into your clamped dewars until full. Wrap towels around the top and tuck into trap clamps to secure. Your pressure meter should read less than 40 mtorr.
5) Put on some heat gloves and grab your glassware from the oven. Grease all joints with vacuum grease while assembling your glassware setup. Be sure to push firmly and twist joints to ensure a good seal (you should be able to see the grease completely coat the joint when it is fully sealed). Once achieved, connect your gas adapter(s) to the Schlenk line using the hoses. If your glassware has cooled, start over. If your glassware is still warm, expose the setup to vacuum. Leave the setup exposed to vacuum until the glassware cools to room temperature (approx 15-20 minutes). This eliminates any surface water adhered to the inside of the glass.

a. It is never a good idea to have more than one system exposed to vacuum at a given time. This leads to gas contamination and to an unreliable pressure reading, in addition to a more frantic search for leaks should one arise.

6) Close the vacuum access port to the system and slowly open the nitrogen access port. This is called backfilling. Evacuate and backfill three times to ensure an all-nitrogen environment, then leave the nitrogen flowing to your system.

a. *To add solid reagents:* Ensure that the system is under a strong nitrogen flow. Open the most convenient access to your system (probably a stopper) and add in the solid reagents.

b. *To add liquid reagents:* If your reaction is not especially air- or water-sensitive, solvents can be added using the above method (be careful of dissolving grease into your reaction mixture). However, if you need to minimize exposure, you can cannulate or syringe-transfer solvent from a bomb flask or other airtight container into your reaction flask.

7) Do chemistry! If you must heat or cool your system, be sure that you have taken the appropriate pressure precautions.

a. If your reaction is very long and you are no longer using your vacuum line, you may want to take down and thaw out your traps. If your reaction is very long and involves the vacuum line, be sure to periodically refill your traps with nitrogen. Another common thing is to see the pressure in the line increasing as you are pulling solvent off on the vacuum line. This is because your traps are too full. Follow the remaining steps as if you were closing down your line, and then go back to step 2.

8) Isolate your system and perform whatever workup/glove box transfer you deem necessary.

9) Close all ports and disable the nitrogen flow.

10) Close the main pump isolation valve. Take down the liquid N_2 dewars, paying attention to the contents of your solvent traps. IF YOU SEE LIQUID O_2, PUT THE DEWAR BACK ON, OPEN THE VACUUM LINE BACK UP, AND TAKE PRECAUTIONS. If everything is okay, let sit for a minute or two, and then slowly open the system to ambient using the vent valve. It is best to immerse the solvent traps in a water bath to aid in thawing. Once the solvent traps have thawed, remove them by disengaging the clamps, empty the trapped solvent into the waste, and clean the traps with acetone and a stream of nitrogen. Go get coffee while your dewars thaw – you're done!

Author and Date: Benjamin Klepser January 19, 2012
Last Revised: Aaron Proctor February 3, 2017
Reviewed and Approved: Bart M. Bartlett February 3, 2017

USING THE GLOVEBOX

Entering the Glovebox:

Items intended to enter the gloveboxes can enter through two antechambers (large and small). The individual ***must*** fill out the glovebox log located on top of the large antechamber. To fill out the glovebox log, note the date, time, initials, which antechamber materials are entering/exiting, the blower pressure and whether the catalyst is open or not (denoted "20/Y" where 20 is the blower pressure and Y or N denotes the circulator is open or not, respectively). When materials have been brought into the glovebox, an individual entry should be marked as done with a check at the end of the line.

All chemicals entering the glovebox ***must*** be degassed and rigorously dried. All glassware entering the glovebox ***must*** also be dried in the drying oven. All empty vessels and dried solids should be vented so no positive pressure is created inside a flask. If a liquid or a flask containing dry reagents is entering the glovebox in a sealed vessel, the vessel must be evacuated on a schlenk line prior to placing in the antechamber. **This is an explosion hazard.** If a vessel is sealed at atmospheric pressure, when the antechambers are evacuated to nearly 0 torr the glassware will likely explode due to the extremely high positive pressure within the flask compared to outside the flask. **Unopened** chemicals packaged under an inert atmosphere may be brought directly into the glovebox. Kimwipes should be dried in the vacuum oven for several hours (>3 h) after the sides of the box have been opened and the plastic opening has been removed (this ensures complete drying of all the Kimwipes).

Aqueous solutions, alcohols, acetone, syringe needles, razor blades, and other sharp objects may never be brought into the glovebox. As they compromise glove lifetime and/or the H_2O/O_2 free atmosphere.

Note: Syringe needles may be brought in if absolutely necessary. Handle with care, as replacement gloves are expensive. Properly store and dispose of any unused and used needles.

Entering the small antechamber:

When bringing items into the glovebox through the small antechamber, *it is imperative that the chamber has been evacuated at least 15 minutes if an item has been removed through that chamber (this can be determined by checking the log)*. Refill the evacuated chamber by turning the valve from "Evacuate" to "Refill." The pressure in the chamber will rise to atmospheric pressure. Turn the valve to "Off" and open exterior of the chamber to insert materials. After closing the chamber, turn the valve cautiously to "Evacuate." Be patient when turning the valve so the pressure decreases slowly. This will reduce the likelihood of glassware shattering if there is a small positive pressure within a flask. After evacuating 3 minutes, turn the valve to "Refill" to

refill the chamber until the chamber is nearly returned to atmospheric pressure. Before the pressure gauge reaches 1 atm, return the valve to “Evacuate” and evacuate the chamber slowly as before. Repeat the evacuate/refill procedure at LEAST 5 times.

Entering the large antechamber:

The large antechamber should be used for items that do not fit into the small chamber. *If an item has recently been removed from the large antechamber (on the log), the chamber must be evacuate for 1 hour prior to bringing anything new into the glovebox through the large antechamber.* The touch screen located on the front of the glovebox controls the large antechamber. First, select “Manual Refill” from the “Antechamber” menu. Then open the chamber and place items entering the glovebox into the chamber. An item entering the large antechamber must be evacuated and refilled 3 times for 20 minutes each cycle. This is an automated process controlled through the “Antechamber” menu. Once the evacuate/refill process has been completed, the chamber can be manually refilled and the item(s) can be brought into the glovebox. Finally, the empty chamber should be manually evacuated immediately after emptying the chamber by selecting “Manual Evacuate” from the “Antechamber” menu.

Working in the Glovebox:

All individuals working in the glovebox must remove all jewlery from hands and wrists. White nylon liner gloves must also be worn whenever using the gloves. This preserves the glove lifetime.

When working in the glovebox with solids, the blower should be set to 20 and the circulator should be open. All solid waste should be disposed in the open container labeled “WASTE.” Avoid contacting solid chemicals with the gloves and clean up spills after using solid chemicals.

Secondary nitrile gloves *must* be worn at all times when working with solvents to prevent glove damage. Different solvents and materials affect the purifier catalyst differently. Some catalyst poisons bind irreversibly to the catalyst whereas others bind reversibly. If working with a solvent that binds irreversibly, the blower/circulator **must** be turned to 0/N. If working with a solvent that binds reversibly, the blower/circulator should remain at 20/Y. A list of catalyst poisons is shown below. Reactions running in the glovebox should be stoppered regardless of the solvents being used to reduce atmosphere or catalyst contamination. Minimize the number of different solvents being used in the glovebox to prevent solvent contamination by other solvents in the atmosphere.

Liquid waste should be placed in the capped bottle labelled “Liquid Waste.” The liquid waste bottle should be open for as little time as possible. It is particularly important that the glovebox is set to 0/N when the liquid waste is open for any time as all solutions (including solvents that poison the catalyst) are discarded here.

All chemicals in the glovebox ***must*** be properly labelled with a sticker label on the outside of any vials. When any waste jar is full, it should be removed from the glovebox, emptied, and

reentered into the glovebox using the above stated procedure for bringing items into the glovebox.

Exiting the Glovebox:

Items intended to exit the gloveboxes can exit through two antechambers (large and small). The individual ***must*** fill out the glovebox log located on top of the large antechamber. When materials have been brought out of the glovebox, an individual entry should be marked as done with a check at the end of the line.

To remove items from the glovebox, “Refill” the desired chamber, open the chamber, place in items to be removed and reseal the chamber. Turn the chamber to “Off,” and open chamber outside the glovebox to remove the items. After removing items, reclose the chamber and turn to “Evacuate.”

After Working in the Glovebox:

After working in the glovebox, ensure that all work spaces/glassware used has been thoroughly cleaned or removed for cleaning. Furthermore, if solvents were used and are no longer open to the glovebox atmosphere, the glovebox ***must*** be purged (while the blower/circulator is at the same setting as when the solvent was open). Purging the glovebox is necessary to ensure any chemicals remaining in the atmosphere have been removed prior to reexposing the catalyst to the glovebox atmosphere (see below). After the glovebox has been purged, the blower/circulator should promptly be returned to 20/Y. Record all purging events in the glovebox log.

Examples of Catalyst Poisons:

Reversible poisons (purge 5-10 minutes depending on duration of solvent use)
- Ammonia
- Ethers (diethyl ether, THF, petroleum ether, hexanes)

Irreversible poisons (purge at least 15 minutes depending on duration of solvent use)
- Sulfur- and phosphine-containing compounds
- Halogens
- Alcohols (or other acidic protons)
- Hydrazine
- Heavy metals (like mercury)
- Amines (especially pyridine)

Emergency Glove Isolation

In the event of a large hole created in a glove during work (due to broken glass, for example), the glove box will rapidly be exposed to ambient atmosphere. In this situation, the glove port can be sealed using the emergency seal door, preventing further compromise of the N_2 atmosphere. The emergency seal door is located on the ceiling of the glove box. Hold the door by the black knob and pull it into the port which holds the affected glove. The door should fit into the port snugly. Turn the black knob (which is now inside the glove port) to the right until the door clicks

shut; you will notice that the plastic latches are now pressed against the inside of the glove and you can no longer push the seal door outwards. At this point, exit the glove box and find the vacuum valve for the seal door on the top of the box (outside). This can be done by following the blue hose from the seal door to the ceiling of the glove box. Open the valve. Lastly, pull the grey cylindrical switch on the outside of the seal door (which is facing the interior of the glove box) upwards to activate the vacuum. The glove is now isolated from the rest of the box. Consult the glove box user's manual for appropriate glove change procedures. In case the solenoid valve stops working and there is a large pressure build-up (gloves will be swollen as a result) immediately turn the high pressure N_2 valve on top of the right side of the glovebox to the off position (horizontal).

Author and Date: Emily Nelson January 20, 2012
Last Revised: Andrew Breuhaus-Alvarez February 2, 2017
Reviewed and Approved: Bart M. Bartlett February 9, 2017

USING THE SOLVENT PURIFICATION SYSTEM

All these directions and more information on troubleshooting can be found in the Solvent Purifier User Guide in the filing cabinet in the group room filed under solvent system.

General lab PPE is required whenever working with the solvent system.

Prior to removing the desired solvent from the solvent system, ensure the solvent has been cycled through the purifier overnight to ensure proper solvent purity. To circulate solvent flip the pump switch from off to on for the desired solvent.

Drying the receiving flask (RF)

Check to ensure the receiving bomb flask does not contain any cracks or hairline fractures. Make sure to pay special attention to the joints and chem thread neck. Ensure the Teflon plug fits securely on the chem thread and forms a seal with the glass at the neck. Dry the RF in the glass oven for at least 30 minutes, preferably overnight.

Starting the Solvent Dispenser

Turn the vacuum pump, located on the far right side of the dispenser table on. The pump will be noisy but should not make a rattling noise. If a rattling noise occurs at start up or appears later, turn the pump off as soon as possible to avoid further damage (it is most likely a loose or broken set screw on the crank shaft of the pump, this has broken previously and can be easily replaced). Allow the pump to run for about 5 minutes. On the solvent desired turn V1 (the top black knob) to inert gas position, then turn V2 (the lower black knob) towards the right. Allow the dispensing spout to purge for at least 3 minutes.

Dispensing the Solvent

Attach the RF to the dispensing spout making sure to secure the RF with a cork ring and jack. Once the RF is secured move V1 towards the vacuum, keep V2 pointing towards the right. Allow the flask to evacuate for 5 minutes. Next, turn the V1 towards inert gas to refill the RF. Repeat the evacuation and refill step three times (the flask must be under vacuum for a total of 15 minutes to ensure adequate removal of moisture and oxygen). After the last refill evacuate the recovery flask one last time for 5 minutes. To dispense the solvent turn V1 to the off position (VERY IMPORTANT!), then turn V2 left to the solvent position. Once the desired volume of solvent has been dispensed, turn V2 toward the off position. If the solvent stops or slows before the desired amount has been dispensed, evacuate the flask briefly by turning V2 towards the right and V1 towards vacuum (make sure to turn V1 back to off before moving V2 left to the solvent position. NOTE: Each solvent will dispense at different rates due to a variety of factors, never walk away from the RF without first examining the flow rate and always check the RF every 5 to 10 minutes to ensure it does not become over filled. Once the desired volume of

solvent has been dispensed, move V2 towards the right and move V1 towards vacuum. Evacuate the RF for 2 minutes to degas the solvent. If the solvent is to be brought into the glove box close the Teflon plug, make sure you see the seal with the glass, and then move V1 to the inert gas position. Slowly lower the jack and remove the RF. Turn V2 and V1 to off and turn off the vacuum pump. Record how much and which solvent you dispensed in the notebook.

If no solvent flows in to the RF first make sure a vacuum was pulled on the flask. Next check the solvent system notebook too see how much of the solvent has been used since the last refill if close to 3 L has been dispensed it is time to refill the reservoir. If the reservoir is still relatively full you can turn on the circulator (switch located on the upper right corner of each solvent unit) to assist with dispensing into the RF.

Refilling the solvent system

Make sure the circulator is turned off. Open the vent valve at the top of the solvent reservoir and immediately turn the sparge gas valve to on. Remove the vent valve and o-ring seal then insert a funnel into the flange, making sure to leave some space between the glass funnel and the metal flange (this can easily be accomplished with a 24/40 glass joint clip). Slowly pour solvent into the funnel (make sure the solvent being added is from OmniSolv and should be unstabilized). Once the solvent has been added remove the funnel and reattach the vent valve and leave in open position. Allow the sparge gas to flow for a short period. Turn the sparge gas valve to off and immediately close the vent valve. To purify the solvent turn the circulation pump on. The solvent needs to circulate for a minimum of 16 hours to reach the desired purity level. Record in the notebook how much and which solvent was added.

Regular Maintenance

Once a month check the solvent usage and refill solvent reservoirs as needed (once the reservoir has approximately 1 L left). It is also necessary to circulate all the solvents at least overnight to ensure the desired purity of the solvents at all times. Periodically (every three months or during group clean up) inspect all lines, valves, fittings and connections for mechanical integrity and inspect the o-rings that seal the sparge valve and those that seal the inlet adapter to the dispensing spout for solvent damage and replace as necessary. See manual for refill instructions.

Specific safety concerns

When refilling the solvent system avoid breathing in solvent fumes. Always have a filling buddy nearby, especially if filling an anesthetic solvent (ether, chloroform, etc.)

Make sure all RF are sound (no cracks, fractures, ect.) to avoid any glass breakage.

Author and Date: Xiaoguang Hao January 19, 2012
Last Revised: John DiMeglio February 3, 2017
Reviewed and Approved: Bart M. Bartlett February 9, 2017

USING HYDROTHERMAL REACTION VESSELS

1. Before using the hydrothermal reactors, make sure you have the right setup for different brands. Currently Bartlett lab owns 3 types of reactors.

2. For an aqueous reaction environment, the maximum reaction volume is 80% of the volume total. The highest temperature for Parr bomb operation is 240 ^{o} C. The other two PTFE vessels can only go up to 200 ^{o} C. For organic solvent reactions, a maximum volume of 5 mL can be used. No higher temperature than 120 ^{o} C is allowed.

3. For special function as ***acid digestion,*** please refer to the Parr bomb manual in the break room shelf. Loading limits are listed here for Parr acid digestion bomb:

    Maximum inorganic sample: 1.0 gram

    Maximum organic sample: 0.1 gram

    Minimum and maximum nitric acid to be used with an organic sample: 2.5-3.0 ml

4. General purpose acid digestion bomb 4745 (referred from Parr manual)

Bomb number 4745

    Size 23mL

    Recommended temperature 150 C

    Absolute max. temperature 250 C

    Absolute max. pressure, psig 1200

5. Operating Procedure

Always keep the bomb right side up during the assembly and closing operations. Check the ***Bottom Disc*** to be sure that it is installed with the proper side facing upward to provide full diameter support for the liner.

Place the sample and the digestion media in the PTFE cup, attach the cover and then push it down firmly with a twisting motion. Slide the closed liner into the bomb body and push it down as far as it will go. It may be helpful to push the bottom disc upward to meet the liner and thereby prevent air binding between the liner and the disc.

Set the Pressure Plate on the top of the cup cover, if the cup cover has a hole in it place a small piece of copper foil between it and the reaction vessel, add the spring and the upper plate, then attach the screw cup and turn it down firmly by hand. (MoS_2 is always recommended for

lubrication). A firm twist by hand should be sufficient to develop and maintain a tight seal. No wrench or spanner is required when running under 100 C.

Place the bomb in a temperature controlled oven or other heating medium and follow the heating and cooling procedure described in the general instructions. When the reaction is complete, vessels should remain in the oven until they are sufficiently cooled. Do not place hot bombs on top of the ovens or bench top to cool.

6. Any chemical left-over attached on the wall of the PTFE vessel should be eliminated immediately after the reaction.

7. Reactions which are highly exothermic or which release large quantities of gas (such as an oxidant and an organic compound) should not be performed in the autoclave.

Author and Date: Brendan Clifford January 19, 2012
Last Revised: Daniel A. McCurry February 2, 2017
Reviewed and Approved: Bart M. Bartlett February 3, 2017

USING THE CENTRIFUGE AND VACUUM OVEN

CENTRIFUGE SAFETY

Centrifuges are machines used to separate solids from liquids in a suspension. The spinning motion of a centrifuge produces centrifugal forces that separate substances of greater and lesser densities.

The centrifuge must be loaded carefully balanced. An unbalanced load may present a risk to both the machine and to persons nearby. Centrifuge rotors should never be touched while the rotor is spinning, as they present a significant personal risk when in motion. Another potential hazard is the possible aerosolization of harmful samples during centrifuge operation.

Engineering Controls

If centrifuging hazardous materials, care should be taken to use tightly capped tubes and/or sealable safety cups or rotors that can be loaded and unloaded in a fume hood or biosafety cabinet, depending on the hazard.

Work Practice Controls

- Before using the centrifuge, make sure you attend the centrifuge training session held by OSEH (http://www.oseh.umich.edu/training/index.shtml)
- Two different types of centrifuge tubes are available for use in lab, 50 mL and 15 mL centrifuge tubes.
    - The centrifuge tubes are located in the front of CHEM 2624 and CHEM 2616 labs on the wooden shelves.
- Before using the centrifuge, make sure all compartment holders are clearly attached to minimize damage when operating the instrument at high rpm's.
- In order to avoid warping the inside of the centrifuge, make sure that you always have a counter balance directly across from your sample that has approximately the same weight.
    - This can be done by measuring out the same amount of liquid in both centrifuge tubes.
    - If you are using the 15 mL centrifuge tubes, be sure to use the appropriate compartment holders that are located next to the centrifuge.
- In order to minimize spilling solvents in the centrifuge, make sure that the caps are tightly sealed before operating the instrument.
    - If you are using other solvents besides water, make sure to always be wearing gloves.
- Wear safety glasses. Before operating the centrifuge, make sure that the lid is completely shut.
    - This can be verified by hearing a "click" noise.

- Avoid operating the centrifuge at very high rates (>3200 rpm). This also limits the amount of damage that could be done to the inside of the centrifuge.
    - If you are using a higher rate, reduce the volume in your tubes and perform multiple centrifuge cycles to avoid damaging the rotor.
- If the centrifuge starts to rattle uncontrollably, be sure to IMMEDIATELY stop it and rebalance your samples by adding more/less solvent in the centrifuge tubes.
- It is a good idea to slowly ramp the centrifuge to the max rpm you would like to achieve.
- When centrifugation is complete, do not try to open the lid until the instrument is completely motionless.

If you plan to reuse centrifuge tubes, only reuse tubes that are not visibly warped. Once a tube starts to warp it may explode during centrifugation. Thus if a tube appears warped in any way it must no longer be used in the centrifuge! This is especially a problem if you are using large tubes that have a large mass of material.

Mechanical Failure

Turn off centrifuge immediately and unplug power cord. Do not use centrifuge again until inspected.

Other Information

2017 Revisions adapted from the University of Michigan. http://ehs.umich.edu/wp-content/uploads/sites/37/2016/02/CentrifugeSafety.docx accessed 2 Feb 2017

VACUUM OVEN SAFETY

Systems under vacuum pose a potential for flying glass, exposure to toxic chemicals contained in the vacuum system and fire from solvent release.

Engineering Controls

Do not tightly cap materials as this will create a large pressure difference between the inside of the vessel and the oven interior.

Traps such as a *cold trap* should be used in line with high vapor loads to minimize the amount of volatile chemicals being evacuated. Ensure the cold trap is appropriate for situation and follows all manufactuer and safety guidelines.

Work Practice Controls

- Be aware of labmates' samples in vac oven- ask before stopping the vac/changing the heating scheme. If the vacuum was on when you put your sample in, be sure to leave it on once you remove your sample.
- Label all samples appropriately so that labmates know whom to contact regarding a sample should it spill.
- The vacuum oven is located directly next to the acid hood in the CHEM 2624 lab.
- If you wish to open the door to the vacuum oven, turn off the vacuum located on the side of the hood and open the knob on top of the oven slowly to release the vacuum
    - This needs to be done slowly because powders may be spilled inside the oven if this is done too quickly

- Open the door once the pressure inside the oven is equilibrated with the outside of the oven.
    - If powders did spill onto the door or bottom of the oven, make sure to wipe up the excess powder with gloves on.
- Place your samples inside the vacuum oven and close the door completely until it latches.
- Slowly pull a vacuum to once again minimize the amount of powder that is spilled inside the oven.
    - It may be a good idea to put a Kimwipe over your vial with a rubber band to minimize spilling.
- Make sure your sample is not completely liquid before putting it in the vacuum oven in order to minimize the amount of solvent that gets pumped into the vacuum.
- Make sure to consult other lab members before setting a temperature just in case some samples need to stay at specific temperatures.
    - Set the desired temperature that you would like with the knob on the front of the oven.

Mechanical Failure

Turn off oven immediately and unplug power cord. Do not use oven again until inspected. If it is safe to do so, vent the oven to atmosphere.

Other Information

2017 Revisions adapted from the University of Michigan.

http://ehs.umich.edu/wp-content/uploads/sites/37/2016/02/VacuumPumps.docx accessed 2 Feb 2017

http://ehs.umich.edu/wp-content/uploads/sites/37/2016/02/Pressure-and-Vacuum.docx accessed 2 Feb 2017

Author and Date: Kayla Pyper January 17, 2012
Last Revised: Sam Esarey February 3, 2017
Reviewed and Approved: Bart M. Bartlett February 3, 2017

USING COMPRESSED GAS CYLINDERS

1.0 Material Requirements

1.1 Equipment needed:
Cylinder cart, cylinder secures (wall and bench-top)

1.2 Gases Used in the Bartlett Lab:
Ammonia: 2624
Argon: 2624, 2622
Helium: 2626
10% Hydrogen/ 90% Nitrogen: 2622
Hydrogen: 2624
Nitrogen: 2622
Oxygen: 2626

1.2.1 Hazards associated with gases:

Ammonia: Irritating or corrosive to exposed tissues. Inhalation of vapors may result in pulmonary edema and chemical pneumonitis. Slightly flammable.

Hydrogen: Flammable fuel; can combust with residual organic matter or oxygen.

Oxygen: Oxidizer. Contact with combustible material may cause fire.

1.3 Engineering controls:
Gas closet (location: 2626) equipped with wall restraints, bench mounted restraints.
Compressed gas cylinders must be secured in an upright position away from excessive heat, highly combustible materials, and areas where they might be damaged or knocked over.

Specialized tubing is required for ammonia gas because of the corrosive properties (i.e. an appropriate option would be stainless steel).
Never interchange regulators and hose lines (with one type of gas for another). There are specific regulators that attach to specific gas types. Explosions can occur if flammable gases or organic materials come in contact with oxidizers (e.g., oxygen) under pressure.

1.4 Protective equipment needed:
When exchanging gas cylinders, setting them up, removing or placing regulators goggles, gloves, face shield, lab coat or apron and/or respirator may be required for personal protection depending on the gas and use.

2.0 Procedure:

1. In order to transport a cylinder, a cylinder cart with secures should be used. Unhook the cylinder from the current secure, place it on the cart and secure it. You may then transport the cylinder where needed.
2. Before unhooking the cylinder and bringing it off the cart make sure there is another secure at the place you plan to leave it. Remove the cylinder from the cart and secure it to the restraints. Place cart back in closet in 2626.
3. Next, take off the cylinder cap and transfer yellow tag directly onto the tank in use. Make sure to rip off the bottom portion of the tag which states 'Full'. This will leave the 'In Service' portion at the bottom of the tag. When a tank is empty remove the 'In Service' portion of the tag so that the tag now reads 'Empty'. When removing empty gas cylinder transfer the tag to the cap once it is on.
4. Next, take off the cylinder cap and open the gas cylinder valve slightly and then immediately close it to blow out dirt or debris from the valve assembly. Aim the valve away from the operator and any other personnel present during this operation.
5. Choose the correct regulator labeled for that specific gas type and attach it to the cylinder. Do not use a gas regulator that does not correspond to the selected gas.
6. Always open valves slowly and never force valves open.
7. Attach appropriate tubing to the gas cylinder and make sure it is tightly secured. If the tubing is attached freely, use a hose clamp in order to secure it.
8. Open main cylinder valve first and then proceed to open the regulator valve to set the gas flow rate for your purposes. If you are not sure what an appropriate flow rate might be for assistance.
9. To shut off, close the main cylinder valve first in order to make sure there is not a pressure build up in the regulator. After a few minutes close the valve on the regulator.

Never:

• Drag, roll or slide cylinders
• Lift cylinders by the cap
• Use cylinders as rollers
• Submit cylinders to temperature extremes
• Strike an arc on a cylinder
• Allow cylinders to contact electrical circuits

3.0 Leaks

3.1 Minor Leaks:

Occasionally a gas cylinder or one of its component parts may develop a leak. Most of these leaks occur at the top of the cylinder in areas such as the valve threads, pressure safety device, valve stem and valve outlet. The following information applies to the remediation of minor leaks:

- If possible, verify suspected leaks using a flammable gas detector or soapy water solution (a flame should not be used for detection). **If the leak cannot be stopped by tightening a valve gland or packing nut, emergency action procedures should be initiated and Chris Peters should be notified if during normal business hours at 734-763-4527.**

- For flammable, inert or oxidizing gases, move the cylinder to an isolated, well-ventilated area (e.g., within a fume hood) away from combustible materials. Post signs that describe the hazard.
- For corrosive and toxic gases, move the cylinder to an isolated, well-ventilated area (e.g., within a fume hood) and use suitable means to direct the gas into an appropriate chemical neutralizer. Post signs that describe the hazards.
- If it is necessary to move a leaking cylinder through populated portions of the building, place a plastic bag, rubber shroud or similar device over the top and tape it (duct tape preferred) to the cylinder to confine the leaking gas.

3.2 Major Leaks:
In the event of a large gas release or if an accident takes place in which readily available personal protective equipment (PPE) is inadequate to ensure worker safety, **activate the following Emergency Procedures**:

- **Immediately call 911** and report the incident.
- Activate building and area fire alarms (or chemical safety alarms if applicable).
- Evacuate the area, securing entrances and providing assistance to others on the way out.
- Provide emergency response officials with details of the problem upon their arrival.

4.0 Storage:
Cylinders must be stored in dry, well-ventilated areas. Cylinders must be stored with the protective caps in place. Under no circumstances should a researcher purchase more than a 4-year supply (the normal course of a research project).

Be aware of incompatibility with other gases already in use in the lab. For example, cylinders of oxygen and other oxidizers must be stored at least 20-feet from fuel-gas or other combustible materials unless separated by a noncombustible wall, not less than 5-feet high, having a fire-resistance rating of 1⁄2-hour.

5.0 Empty Cylinders:

Cylinders are considered "empty" if their pressure is less than 25 psi and should then be placed in 2626 using the same procedure as mentioned in 2.0. The tag should also then read “empty.”

6.0 Accident Procedures: (Found in the MSDS)

6.1 Contact

Ammonia
6.1.1 Skin: Remove contaminated clothing as rapidly as possible. Flush affected area with copious quantities of water. In cases of frostbite or cryogenic "burns" flush area with lukewarm water. DO NOT USE HOT WATER. A physician should see the patient promptly if the cryogenic "burn" has resulted in blistering of the dermal surface or deep tissue freezing.
6.1.2 Eyes: Flush contaminated eye(s) with copious quantities of water. Part eyelids to assure complete flushing. Continue for a minimum of 15 minutes. PERSONS WITH POTENTIAL EXPOSURE TO AMMONIA SHOULD NOT WEAR CONTACT LENSES.

6.1.3 Inhalation: PROMPT MEDICAL ATTENTION IS MANDATORY IN ALL CASES OF OVEREXPOSURE. RESCUE PERSONNEL SHOULD BE EQUIPPED WITH SELF-CONTAINED BREATHING APPARATUS. Conscious persons should be assisted to an uncontaminated area and inhale fresh air. Quick removal from the
contaminated area is most important. Unconscious persons should be moved to an uncontaminated area, given mouth-to-mouth resuscitation and supplemental oxygen. Keep victim warm and quiet. Assure that mucus or vomited material does not obstruct the airway by positional drainage.
6.1.4 Ingestion: Not specified. Seek immediate medical attention.

Argon
6.1.1 Skin: None expected.
6.1.2 Eyes: Check for and remove any contact lenses. Immediately flush eyes with plenty of water for at least 15 minutes, occasionally lifting the upper and lower eyelids. Get medical attention immediately.
6.1.3 Inhalation: Move exposed person to fresh air. If not breathing, if breathing is irregular or if respiratory arrest occurs, provide artificial respiration or oxygen by trained personnel. Loosen tight clothing such as a collar, tie, belt or waistband. Get medical attention immediately.
6.1.4 Ingestion: As this product is a gas, refer to the inhalation section.
6.1.5 Frostbite: Try to warm up the frozen tissues and seek medical attention.

Helium
6.1.1 Skin: No harm expected.
6.1.2 Eyes: No harm expected.
6.1.3 Inhalation: Immediately remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, qualified personnel may give oxygen. Call a physician.
6.1.4 Ingestion: This product is a gas at normal temperature and pressure.

Hydrogen
6.1.1 Skin: No harm expected
6.1.2 Eyes: No harm expected
6.1.3 Inhalation: Persons suffering from lack of oxygen should be removed to fresh air. If victim is not breathing, administer artificial respiration. If breathing is difficult, administer oxygen. Obtain prompt medical attention.

Nitrogen
6.1.1 Skin: No harm expected.
6.1.2 Eyes: No harm expected
6.1.3 Inhalation: Persons suffering from lack of oxygen should be moved to fresh air. If victim is not breathing, administer artificial respiration. If breathing is difficult, administer oxygen. Obtain prompt medical attention.
6.1.4 Ingestion: This product is a gas at normal temperature and pressure.

Oxygen
6.1.1 Skin: No harm expected.
6.1.2 Eyes: Check for and remove any contact lenses. Immediately flush eyes with plenty of

water for at least 15 minutes, occasionally lifting the upper and lower eyelids. Get medical attention immediately.
6.1.3 Inhalation: If inhaled, remove to fresh air. If not breathing, give artificial respiration. Get medical attention.
6.1.4 Ingestion: This product is a gas at normal temperature and pressure.
6.1.5 Frostbite: Try to warm up the frozen tissues and seek medical attention.

10% Hydrogen/90% Nitrogen
6.1.1 Skin: No harm expected.
6.1.2 Eyes: If release of this gas mixture has affected the eyes, seek immediate medical attention.
6.1.3 Inhalation: If inhaled, remove to fresh air. If not breathing, give artificial respiration. Get medical attention.
6.1.4 Ingestion: This product is a gas at normal temperature and pressure.
6.1.5 Frostbite: Try to warm up the frozen tissues and seek medical attention.

6.2 In case of Fire:
Ammonia: If possible, stop the flow of gas. Since ammonia is soluble in water, it is the best extinguishing media--not only in extinguishing the fire, but also absorbing the escaped ammonia gas. Use water spray to cool surrounding containers.
Argon: Apply water from a safe distance to cool container and protect surrounding area. If involved in fire, shut off flow immediately if it can be done without risk.
Helium: Helium cannot catch fire. Use media appropriate for surrounding fire.
Hydrogen: Begin to cool tank from a maximum distance with water spray, taking care not to extinguish flames. If flame is extinguished before cooled, explosive re-ignition may occur. Stop flow of gas and extinguish while continuing water spray after initial cooling. To extinguish, use CO_2, dry chemical, water spray or fog for surrounding area. Do not extinguish until H_2 source is shut off.
Nitrogen: Nitrogen is nonflammable and does not support combustion. Use extinguishing media appropriate for the surrounding fire.
Oxygen: Extremely flammable in the presence of the following materials or conditions: reducing materials, combustible materials and organic materials. Apply water from a safe distance to cool container and protect surrounding area. If involved in fire, shut off flow immediately if it can be done without risk.
10% Hydrogen/90% Nitrogen: Use fire-extinguishing material appropriate for surrounding materials. Use water spray to cool fire exposed structures, cylinders and equipment.

Report all accidents, e.g., injuries, leaks, fires, etc., to the following
Chris Peters: 1608 Chem
Work: 734-763-4527

For emergencies during non-business hours, call the Dept. of Public Safety at 911 (*from any campus phone*) or (734) 763-1311.

Author and Date: Joseph Yourey August 06, 2013
Last Revised: James Brancho January 17, 2017
Reviewed and Approved: Bart M. Bartlett August 6, 2014

USING THE TUBE FURNACE

1.0 Material Requirements

1.1 Equipment needed:

The tube furnace. The tube furnace is an oven used to anneal, calcine, and sinter materials in a controlled atmosphere. The tube is a quartz tube, and the lab usually has two tubes. The tube seals on either end by 1) an input phalange equipped with a 3-way valve which allows the operator to switch between the permanent NH_3 line and a red rubber-tube line which can be attached to various tanks of gases and 2) a clamped gas outlet which is hooked up to an oil bubbler.

There may not be an NH_3 line hooked up as new safety parameters have been put in place for NH_3 gas use by OSEH. However, that spot is still available for other gases hooked to the 3-way valve.

1.2 Gases Used

Please read the SOP section on gas cylinders to familiarize yourself with the dangers of each gas you may want to use if your experiments.

Argon, Nitrogen, Oxygen, 10% Hydrogen/90% Nitrogen: Tanks are secured on bench top and connected with tygon tubing

Hydrogen: Tank is secured on bench top and connected by Tygon tubing.

1.2.1 Hazards associated with gases:

Ammonia: Irritating or corrosive to exposed tissues. Inhalation of vapors may result in pulmonary edema and chemical pneumonitis. Slightly flammable.

Hydrogen: Flammable Fuel; can combust with residual organic matter or any O_2 from leak in system.

1.3 Engineering controls:

Specialized tubing is required for ammonia gas because of the corrosive properties (i.e. an appropriate option would be stainless steel).

2.0 Procedure:

1. Preparing the tube: This procedure begins with a quartz tube, centered in the furnace without any phalanges, insulating blocks, or samples loaded.
    a. 1st, you should completely power OFF the power supply before loading your sample. This is done by pushing the RED rectangular button on the bottom right side of the furnace.

b. You will want to prepare the inlet end of the tube (this is the right side of the tube). 1st, place the alumina insulating block at the end of the heating zone. The right side of the heating zone. This is just beyond the beginning of the metal casing on the furnace. Slide the block into the center using the steel rod.
c. Next, attach the steel phalange to the end of the furnace, tightening evenly and not so hard that you shatter the quartz tube. Then, make sure the valve in aligned to the gas inlet you are using for your experiment.
d. Loading the sample. The sample should be loaded directly in the center of the heating zone to assure accurate temperatures. When looking at the back of the oven, the thermocouple which extend out the back of the furnace is the center of the furnace. Use this as your guide. Then, marking a known distance along the steel rod, push your sample into the tube slowly to the center of the zone.
e. Next, push the second alumina insulating block to the furthest left side of the heating zone. Again, this is approximately at the edge of the metal on the left side of the furnace.
f. Finally, attach the glass phalange to the outlet (left side) and tighten to seal the tube.

2. Preparing for heating
    a. The furnace needs to be purged completely *before* heating to ensure the atmosphere of the tube is uniform. Bubble your gas through the tube (semi-vigorously ~ 10 bubbles/s) for approximately 20 minutes to purge the tube. *When using hydrogen, purge with an inert gas for 20 minutes first, then with hydrogen for 20 minutes longer to ensure all air is completely displaced from the tube.
    b. Now, re-power the voltage supply. Push the GREEN rectangular button.
    c. Next, program the oven. The programming of this tube is the same as the small box furnaces.
    d. After programming, you can beging your experiment.
        i. During your experiment, gases are typically bubbled through at a slow rate, ~1-2 bubbles/s.

3. After your experiment, power off the voltage supply by again pushing the RED button. Next, remove the glass phalange and alumina insulating block. Then, using the hook on the end of the steel rod, catch your crucible and slowly bring out of the furnace.

Special procedures for air-sensitive work

Many tube furnace operations are carried out in flowing air or oxygen. For especially sensitive reactions that need to be carried out in an inert atmosphere, the tube furnace has been equipped with additional purifiers to remove trace air and water from gases. The purifiers are compatible with nitrogen and argon.

The two purifying columns are phosphorous pentoxide (white) and copper metal + copper(I) oxide, 1:1 by weight. The purpose of the phosphorous pentoxide column is to remove trace water from inlet gas. This purifier should come first. The Cu/Cu_2O column removes any

remaining oxygen. It should always be kept on a hot plate in a sand bath, as it is not effective at room temperature.

If you are performing a sensitive reaction (for example, this procedure was optimized for synthesizing titanium nitrides from reactive molecular precursors), the Schlenk line in Hood #_ must be available for use. For nitrogen, the house nitrogen is suitable. For argon, attach an argon tank nearby and run it through the Schlenk line instead of nitrogen.

Procedure:

1. Check the purifying columns for quality. If the phosphorous pentoxide column contains visible amounts of black goo and it does not look like powdered P_2O_5 is sitting between the internal glass tubes, refresh the purifier (see below). Also, check the Cu/Cu_2O column. If it is black, then it has been converted to CuO and needs to be refreshed.
2. Turn the hot plate beneath the Cu/Cu_2O column to 285 °C. This results in a temperature of about 185 °C in the sand bath, at which Cu/Cu_2O is effective at removing oxygen. It takes about 40 min to heat up.
3. Prepare and load your sample according to the procedure above using Schlenk techniques. If your sample can withstand vacuum, it is a good idea to evacuate and backfill the quartz tube and purifiers to eliminate any oxygen introduced during sample loading. Otherwise, we have a specialized quartz tube that can be loaded and sealed on the line or in a glove box, then transferred to the tube furnace with minimal contamination.
4. Run reaction as described above.
5. When finished, stop the gas flow through the manifold using one of the stopcocks but leave gas flowing through the Schlenk line to blanket the purifiers; this extends their life. Turn off the hot plate beneath the Cu/Cu_2O column.

Refreshing the purifiers:

Caution: Phosphorous pentoxide is extremely corrosive and hygroscopic, forming a sticky goo when left exposed to air for a short amount of time. Wear appropriate PPE (gloves, glasses, lab coat) and do not rush.

For the phosphorous pentoxide column, prepare about 500 mL of 1:1 v/v H_2O/ethanol and obtain a new quart jar waste container. Open the purifiers and discard most of the P_2O_5 into the quart jar. The remaining goo can be removed with the H_2O/ethanol solution. This solution reacts vigorously with P_2O_5 – be sure that the large P_2O_5 deposits are transferred to the quart jar before employing the solution. Soak the glass parts in H_2O/ethanol for an hour or until no P_2O_5 residues are visible. Rinse with plenty of water and dry in the drying oven. Refill with P_2O_5 (about 3” from the bottom of the purifier cup is plenty). Plug the glass tubes with cotton to prevent powder from flying during Schlenk operations. Leave the dry P2O5 open to air overnight; it will absorb enough water from the air to become a less reactive liquid the next day (phosphoric acid). It is now safe to add the H_2O/ethanol to the waste jar and dispose along with any contaminated wipes.

For the Cu/Cu_2O column, discard the spent material in a solid waste bucket. If necessary, you may soak the glass pieces in 6 M hydrochloric acid or aqua regia to remove copper from the joints or o-ring seats. Rinse, dry in the drying oven. Grind together about 20 g of Cu and 20 g of Cu_2O, then add to the dry column. Plug the glass tubes with cotton to prevent powder from flying during Schlenk operations.

After refreshing either purifier, evacuate and backfill using Schlenk techniques for at least 3 h. The powders are porous and it takes a while under vacuum for the atmospheric gases to desorb.

Author and Date: Kayla Pyper January 17, 2012
Last Revised: Adam Crowe February 2, 2017
Reviewed and Approved: Bart M. Bartlett February 3, 2017

GLASS CUTTING AND USING FLUORINATED TIN OXIDE

1.0 Material Requirements

1.1 Equipment needed:

FTO sheets on soda-lime glass (usually 12 x 12 sq inch), diamond cutter, ruler, thin marker, paper weight, wood jig, piece of paper with small film dimensions.

1.2 PPE:

Goggles and gloves must be worn.

2.0 Procedure:

1. Make sure you are wearing gloves and goggles.
2. Obtain a piece of FTO from under the counter in 2624 and rinse it off with water to clean it up. Dry it.
3. Lay out a paper towel covering the bench-top to lay the glass on.
4. Use the multimeter on the setting that looks like a little internet symbol and place the two tips on the glass to identify the FTO side.
5. Once you have identified the FTO make sure this side is FACE DOWN.
6. Use the ruler and thin marker and draw a vertical line directly down the middle of the glass. Follow that marker line with the diamond cutter while keeping the ruler steady. Place sufficient pressure on the glass while pressing the diamond cutter to the surface. The most efficient way to use the diamond cutter is to have a firm grip on the cutter and putting pressure on the glass. Make sure the scribe is in contact with the glass.
7. Break this piece in half.
8. Take one of the pieces and turn it so short side is now perpendicular to the edge of the bench top. Use the weight as a stop on the right side and place the wood jig on the left hand side of the glass.
9. Use the diamond cutter to cut the glass and break off each piece accordingly. Keep doing this until you are finished with that piece and repeat on the other piece.
10. Keep doing this until you are finished with that piece and repeat on the other piece.
11. Take the smaller pieces and line them up with the template on the piece of paper and cut them into thirds accordingly.
12. Once all of that is finished you are done. Put everything back where you found it.
13. To clean the FTO, sonicate in ethanol and acetone for 10 minutes make sure to agitate the solution periodically to separate the FTO pieces. Finally, sonicate with H_2O and then rise with H_2O. Towel Dry.

2.1 Hazards associated with cutting FTO:

DO NOT cut yourself with the FTO, it can be sharp.

3.0 Accident Procedures:
If you cut yourself or get injured using any of these materials make sure to clean out the wound and appropriately use the first aid kits located at the entrance to lab 2624 or 2616.

Author and Date: Tanya Breault January 19, 2012
Last Revised: Aaron Proctor February 3, 2017
Reviewed and Approved: Bart M. Bartlett February 3, 2017

USING THE THINKY ROTATION/REVOLUTION SUPERMIXER

- The manual is located in the file cabinet in the break room.
- Caution and Safety:
    - Wear safety glasses when near machine incase inner pieces were to malfunction and disassemble.
    - Don't start machine with door opened.
    - Don't use solvents near machine since leaks/splashes could deteriorate parts of machine and cause breakage.
    - Don't mix hazardous or toxic materials in Thinky mixer
    - Machine is not suited for anti-blasting
        - Handle with care, as fire, explosion due to vaporization, and temperature rise by chemical reaction can cause problems
- Cups and glass balls are located in a marked drawer Lab 2642
- After making your desired slurry mixture, weigh cup such that you can adjust the balance within the mixer to the appropriate weight
- Surround the cup with pig mat and/or bubble wrap so that it snugly fits into the mixer
- In the case of abnormal vibration or noise, stop mixer immediately and inspect contents, look for leaks, etc.
- The maximum stir time is **10 min**
    - If your slurry requires longer mixing, allow the cup to cool down before the next 10 min cycle. This prevents the cup from overheating and melting to the holder cup. If the cup melts in the holder, parts can become damaged, resulting in the machine breaking.

Author and Date: Tanya Breault — January 19, 2012
Last Revised: Andrew Breuhaus-Alvarez — February 2, 2017
Reviewed and Approved: Bart M. Bartlett — February 9, 2017

ORDERING CHEMICALS AND SUPPLIES

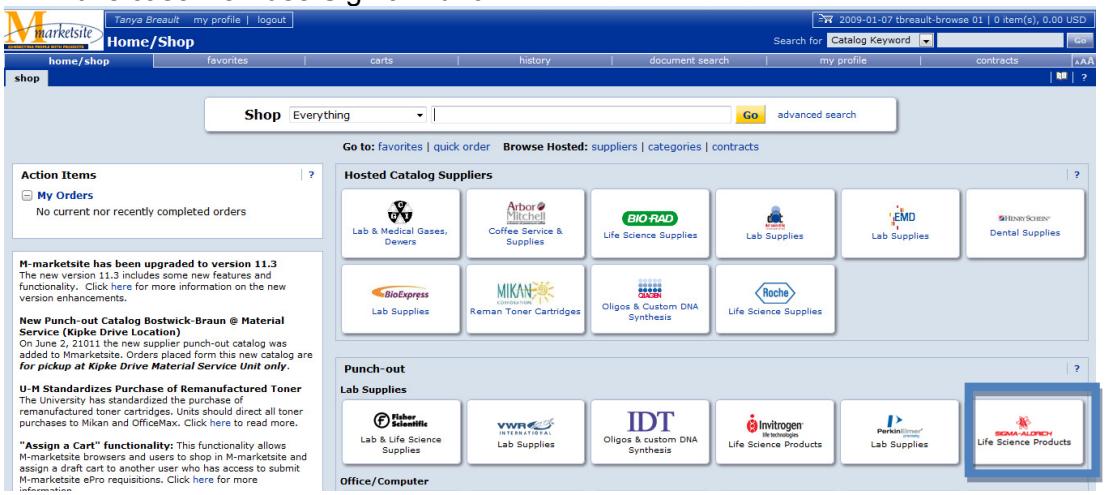
- Orders are placed each morning around 10am, if you absolutely need an order placed on a day later than that, please notify Sam and he will place the order.
- Look up prices for chemicals/supplies through the University punch out. Prices listed here are usually cheaper than those if you were to just look on the supplier's website.

1. Go to Wolverine Access > Faculty and Staff > M-Marketsite Browse Only:

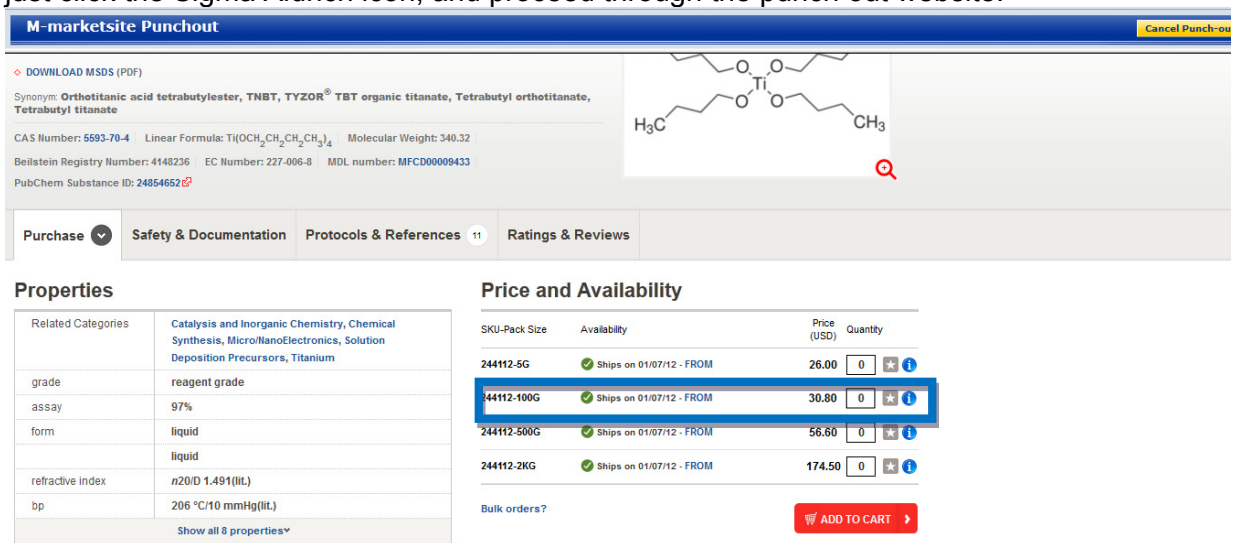
Click here!

2. Enter log in information: Umich Kerberos ID and password
   - Rotators do not have access, so ask a senior lab member for assistance

3. You should now be at the punch out section, so click on supplier you are interested in. In this case we'll use Sigma Aldrich.



4. For example, if looking for the chemical titanium butoxide through Sigma Aldrich, just click the Sigma Aldrich icon, and proceed through the punch out website:



- The information you will need to record in the excel sheet includes the catalog/SKU number, quantity, and price.

5. On the group computer, there is an excel sheet labeled "Bartlett Group Inventory" located on the Desktop. Click on this to enter the date, your name, company, catalog number, item description, quantity, type of quantity, and price for each product you are ordering on the "order" tab.
   - Be sure to spell out the full chemical name, do not abbreviate anything. Include mass/volume of chemicals with item description
     - PEG = polyethylene glycol, 500 g
     - TiO_2 = titanium dioxide, 100 mL

- When searching for a chemical through the punchout, order through company logo you click
    - Fisher > Acros…You may find a chemical from across, however since you went through the fisher punchout, you'll enter in excel as a *Fisher* product

6. The excel sheet contains several other useful tabs:
    - *Order*- where you enter your request for an item to be ordered.
    - *Ordered*- lists dates of previous chemicals ordered. Check here for catalog numbers to look up current prices through the punch out.
    - *Ordered 2014*- lists dates of previous chemicals ordered in the year 2014. Check here for catalog numbers to look up current prices through the punch out.
    - *General lab supplies*- contains a list for each punch out site with catalog numbers for supplies ordered often.
    - *Company info*- lists companies that supply "odd" items, with all contact information one would need to contact the company.
        - MTI- furnace items
        - Cryogenic gases- various gas cylinders
    - *Passwords*- in case you forget a password to a group computer, you can find them here, as well as in the drawer near the group computer in the break room.
    - *Peroxidizables*- dates that peroxidizables were tested, and status of each test.
    - *Glove box chemicals*- list of chemicals located in glove box for your convenience.

7. Typical starting places when searching for a certain chemical/lab supply:
    - Chemicals: Sigma-Aldrich, Fisher, VWR, Strem (does not have punch-out, see website: http://www.strem.com).
    - General lab supplies: Fisher Scientific
        - ORDER **BEFORE** THEY RUN OUT
        - If you take the last of something (a box of scintillation vials), place an order that day so that it is replenished before a lab mate needs that item
    - Office supplies: OfficeMax
    - Gases: Cryogenics/Metro welding (you can find their prices through wolverineaccess, just search for the item part number and it will show).
    - Furnace accessories: MTI corporation
    - Deuterated solvents: Cambridge isotopes ($50 minimum), list on wall has prices
    - Alcohol: list on wall has prices
    - **Search each website to find best price for the purity and quantity needed.**

8. Please try to order from preferred vendors whenever possible (the vendors listed through the M-marketsite). They will often waive hazardous materials and shipping fees (Fisher does this especially). So if the difference in price between a preferred vendor and another place is <$20 then you should order it from the preferred vendor because the total cost will be less due to the subtraction of certain fees,

Author and Date: Tanya Breault — January 19, 2012
Last Revised: Bart Bartlett — February 9, 2017
Reviewed and Approved: Bart M. Bartlett — February 9, 2017

DATA BACK-UP AND MANAGEMENT

1) All laboratory experiments (syntheses and descriptions of how characterization data are collected) are recorded in the Elements electronic notebook, available online at https://elements.perkinelmer.com/.
2) Raw data on networked computers will be written *directly* to a stored drive: \\lsa-research05.m.storage.umich.edu\lsa-research05\bartmb.
3) Co-workers store worked up data from the group computer as well as personal computers to the network drive above.
4) Working copies of manuscripts and proposals with the original artwork and worked-up data are stored in Dropbox, available online at https://www.dropbox.com/
5) Bart stores archived copies of finished work in M+Box, available online at https://umich.app.box.com/
6) Co-workers are responsible for securing data collected from instrumentation around campus (e.g.—XRD patterns, SEM images, XPS analysis) and backing them up to the stored drive listed above.

Author and Date: Aaron Proctor January 26, 2016
Last Revised: Daniel A. McCurry February 2, 2017
Reviewed and Approved: Bart M. Bartlett February 1, 2016

WORKING WITH HYDROFLUORIC ACID

Before lab personnel work with hydrofluoric acid, they must get prior approval from Professor Bart Bartlett. They must also complete online training. This can be found through My Linc on Wolverine Access. The course code is BLS026w (titled "BLS026w - ONLINE REQUIRED Hydrofluoric Acid and Ammonium Fluoride Safety in the Laboratory"). They also need to review the OSEH SOP for working with Hydrofluoric acid.

Brief Background

Hydrofluoric acid (HF) is a highly corrosive liquid and is a contact poison. It should be handled with extreme care (i.e., beyond what is generally required to handle other mineral acids). Owing to its low dissociation constant, HF as a neutral lipid-soluble molecule penetrates tissue more rapidly than typical mineral acids. Because of the ability of hydrofluoric acid to penetrate tissue, poisoning can occur readily through exposure of skin or eyes, or when inhaled or swallowed. Symptoms of exposure to hydrofluoric acid may not be immediately evident. HF interferes with nerve function, meaning that burns may not initially be painful. Accidental exposures can go unnoticed, delaying treatment and increasing the extent and seriousness of the injury.

HF is a calcium seeker. A person can't sense when it comes in contact with the skin. But, it dissolves the calcium in the bone. HF burns are not evident until a day later. If not stored, handled and disposed of properly, HF can pose a serious threat to the health and safety of laboratory personnel, emergency responders and waste handlers. Hence, it is important to thoroughly understand the properties of HF and follow all safety protocols to properly store and handle HF.

Engineering Controls

Any work with HF must be done in a chemical fume hood. An eyewash/drench hose combination unit must be available in the immediate work area for any work with corrosive materials. For many uses of HF, an eyewash station and a safety shower will also be necessary. Provide exhaust ventilation or other engineering controls to keep the airborne concentrations of vapors below their respective threshold limit value (3 ppm as an 8-hour time-weighted average).

Work Practice Controls

- Consider alternate methods and use a less dangerous acid if possible.
- Designate areas where HF is stored and manipulated.
- Purchase HF in the smallest amounts possible.

- Stock calcium gluconate gel to be used as first aid in case of an HF burn. (Medical attention must still be sought immediately for HF burns.) Prior to using HF, make sure the calcium gluconate tube is unopened and that the gel has not reached the expiration date stamped on the tube.
- Do not heat hydrofluoric acid.
- Do not use glass, ceramic, or other incompatible containers for HF.
- Perform a dry run to identify and correct potential hazards.
- Add acid to water, not water to acid.
- Work within sight and/or hearing of at least one other person who is familiar with the hazards and written procedures.
- Line work surfaces with plastic-backed absorbent paper and/or a containment tray of compatible material.
- Once work with HF is complete, decontaminate the area by wiping it down with a 10% sodium carbonate (Na_2CO_3, also known as soda ash) solution.
- Gaseous hydrogen fluoride:
  - Follow SOP for compressed gas guideline.
  - If you have any HF in glass containers, be aware that it can be extremely dangerous. Contact OSEH Hazardous Materials Management (OSEH-HMM) at (734) 763-4568 for an immediate pickup.

Minimum PPE:

1. Safety glasses that completely shield the eyes from splashing
2. Nitrile gloves underneath larger neoprene gloves (usually next to base bath)
3. Lab Coat

Special Note Handling Note – Do NOT Work Alone

Never work with HF alone. Another lab mate versed in the SOP of HF should be nearby, ready to apply Calgonate gel or eyewash according to the below first aid procedures, if necessary.

First Aid Procedure

If the employee is in need of emergency medical attention, call 911 immediately

For an actual chemical exposure/injury:

- In case of SKIN exposure, remove contaminated clothing from affected area. Rinse with water for **5** minutes. Immediately after rinsing, use a ***gloved*** hand to apply calcium gluconate gel to the skin and rub it in. Seek medical treatment below.
- In case of EYE exposure use Calgonate Emergency Eyewash immediately. Call 911. NOTE: Do not open the Calgonate Emergency Eyewash Solution container seal, unless needs to be used. Use the entire 120 ml content during an emergency (eye exposure). Calgonate Emergency Eyewash Solution is for single use only.

- For situations with risk of inhalation exposure (including spills of powder outside of a chemical fume hood), remove all persons from the contaminated area and contact OSEH-HMM (734) 763-4568.
- If an ambulance is needed, call the University of Michigan Police Department (UMPD) at 911 to request assistance.

Contact OSEH for advice on symptoms of chemical exposure, or assistance in performing an exposure assessment.

Report all work related accidents, injuries, illnesses or exposures to WorkConnections within 24 hours by completing and submitting the Illness and Injury Report Form. Follow the directions on the WorkConnections website Forms Instructions to obtain proper medical treatment and follow-up.

Complete the OSEH Laboratory Incident and Near-Miss Report form.

TREATMENT FACILITIES:

U-M Occupational Health Services -- *Campus Employees*
Mon-Fri 7:30 am - 4:30 pm
After hours - go to UM Hospital Emergency Dept. – Urgent Care Clinic
C380 Med Inn building
1500 East Medical Center Drive, Ann Arbor (734) 764-8021

University Health Services -- *University students (non-life threatening conditions)*
Mon-Fri 8 am – 4:30 pm, Sat 9 am – 12 pm
Contact for current hours as they may vary
207 Fletcher Street, Ann Arbor (734) 764-8320

UMHS Emergency Department -- *after clinic hours or on weekends*
1500 East Medical Center Drive, Ann Arbor, (734) 936-6666

Spill Procedure

- When a spill occurs, ***personal safety should always come first.***
- Alert and clear everyone in the immediate area where the spill occurred.
- On the UM campus, any spill of more than 5 ml of hydrofluoric acid must be referred to OSEH-HMM by calling (734)763-4568 from any phone.
- Spills of HF in the fume hood (<5 ml) can be absorbed using magnesium sulfate, soda lime, sodium carbonate (Na_2CO_3), or other spill absorbent specified for HF. Do NOT use organic spill kits that contain Floor-Dri, kitty litter, or sand because HF reacts with silica to produce silicon tetrafluoride (a toxic gas). After spill has been completely absorbed, wipe down spill site with 10% sodium carbonate solution.

If any large Hydrofluoric Acid solution is spilled, leave the lab and call UMPD at 911 to request assistance from OSEH. Do not take any action to cover the spill. Post a warning on the

lab and do not allow others to enter. Have a person available that has knowledge of the incident and laboratory to assist emergency personnel.

Transportation and Storage

- Transport corrosives in secondary containment, preferably a polyethylene or other non-reactive acid/solvent bottle carrier.
- Store in a compatible container (preferably polyethylene). HF reacts with glass, ceramics, and some metals.
- Place it in a compatible secondary container to capture leaks or spills.
- Store with other inorganic acids, away from bases and other incompatibles including metal (unless the metal has a corrosion-proof coating), and do not store under the sink.
- Avoid storing on the floor.
- Store in a cool, well-ventilated areas.
- Store below eye level.
- Store away from incompatibles.

Waste

A polyethylene waste bottle should be acquired from Laurie MacDonald (1614 Chemistry, (734)764-7325 lanald@umich.edu). This should be kept in secondary containment. This can be placed in solvent closet for waste pickup as normal.

Hydrothermal Reactions with HF

If performing a hydrothermal reaction (i.e. heating sealed Teflon-lined autoclaves), a sign should be put on the oven indicating that the bombs it is holding contain HF. **BE SURE THE VENTILATION SYSTEM ON THE OVENS IS CONNECTED PROPERLY BEFORE HEATING THE BOMBS.**

Other Information

2017 Revisions adapted from the University of Michigan. http://ehs.umich.edu/wp-content/uploads/sites/37/2016/02/HydrofluoricAcid.docx accessed 2 Feb 2017

Author and Date: Charles Lhermitte July 08, 2015
Reviewed and Approved: Bart M. Bartlett February 1, 2016

PREPARING AN AQUEOUS Ag/AgCl ELECTRODE

Electrode prep: Clean the silver wire with a fine grade emery paper (sand paper, 600 grit is fine) and rinse it with distilled water. Make sure that only bare silver is exposed, you do not want any residual deposits from the previous AgCl layer. Insert the part to be coated into 0.1 M HCl and pass 10 mA/cm^2 for about 1 min, using a platinum wire as a cathode/reference. During the electrolysis a black deposit is formed on the silver. Rinse the electrode with pure water then dry with N_2. Insert it into a glass tube with Vycor frit tip that was previously filled with an aqueous sat'd KCl solution. Before use place the reference electrode in a beaker with sat'd KCl for a few hours to reach a stable potential. When not in use store the electrode in sat'd KCl. The potential of an electrode prepared as above is within ±1 mV of the expected value[1].

References:

[1]: Electrode preparation adapted from: http://www.tau.ac.il/~advanal/ReferenceElectrode.htm