UMDNJ
UNIVERSITY OF MEDICINE & DENTISTRY OF NEW JERSEY

ENVIRONMENTAL AND OCCUPATIONAL HEALTH AND SAFETY SERVICES

STANDARD OPERATING PROCEDURES

Safe Work Practices for the Use of Pyrophoric and Highly Reactive Chemicals in the Laboratory

Effective Date: April 16, 2010	**Revision Date:**

INSTRUCTIONS The Responsible Investigator should ensure that laboratory personnel review this Standard Operation Procedure (SOP) in conjunction with hands-on training if they will use pyrophoric or highly reactive chemicals. All personnel who may be in the room when the materials are used must be familiar with the emergency procedures listed in this SOP. Training sessions should be documented using the Training Sheet at the end of this document.

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1.0 PURPOSE

This standard operating procedure (SOP) is intended to provide general guidance on working with pyrophoric and highly reactive chemicals in a manner which minimizes the risk of fire/explosion, injury, and exposure.

2.0 OVERVIEW

In 2009, a young UCLA research associate died from burn injuries sustained in a research laboratory fire. The victim was using a syringe and needle to extract a pyrophoric chemical (t-butyl lithium) from a bottle. The plunger came out of the syringe barrel and the t-butyl lithium ignited on contact with room air. The chemical splashed onto the victims clothing and set them on fire. She was not wearing a laboratory coat at the time of the incident. There was no written documentation that the victim had received formal training on the safe use of pyrophoric chemicals. A report of the incident is posted at: http://www.cdph.ca.gov/programs/ohb-face/Documents/09CA001.pdf. The practices and laboratory procedures described below are intended to reduce the risk of a similar incident occurring at UMDNJ.

Laboratory workers should attempt to manipulate pyrophoric materials, only after implementing this SOP and receiving documented training. The potential hazards should be thoroughly researched and where appropriate knowledgeable peers should be consulted with regard to the correct laboratory techniques Failure to follow proper handling precautions can result in the exposure of these materials to the atmosphere, with consequences including serious injury or death.

3.0 IDENTIFYING PYROPHORIC AND REACTIVE CHEMICALS

Pyrophoric chemicals are liquids or solids that will ignite spontaneously in air. Many of them are also water reactive and will ignite upon contact with water (or even air which normally contains some moisture). Pyrophoric materials are usually manipulated in an inert (non-reactive) atmosphere of nitrogen or argon using specialized glassware. Many reagents are supplied diluted in a flammable organic solvent such as hexane.

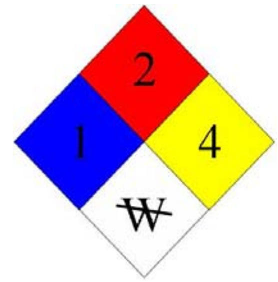
Some of the most common pyrophoric lab reagents include chemicals that contain functional groups such as:

- organolithium (lithium aluminum hydrides, lithium nitride)
- organozinc, such as diethylzinc
- organomagnesium (Grignard reagents)
- aluminum alkyls, such as trimethyl aluminum
- metallic hydrides, such as sodium hydride, potassium hydride, lithium aluminum hydride and some boranes

Also, finely divided metals, such as aluminum, lithium, magnesium, titanium, zinc, zirconium, sodium, and potassium, are pyrophoric.

Pyrophoric reagents can be identified in a number of ways. The warning label on each container will include a symbol indicating water contact should be avoided (see below, next page). The NFPA reactivity classification will also be ranked as “3” or “4.” The

Material Safety Data Sheet (MSDS) will describe the material as "highly flammable" and/or "pyrophoric," and it may also include a list of some incompatible mixtures



The hazards that stem from these chemicals are caused by the combination of spontaneous ignition on contact with air and water, along with the flammability.

4.0 HANDLING PYROPHORIC CHEMICALS

4.1 Solid pyrophorics must only be handled in an inert atmosphere glove box. Less expensive, inert atmosphere glove bags are also available by key word-searching "inert atmosphere glove bags" on the internet or by going to UMDNJ Marketplace for the Fisher Scientific Vendor. Fisher Scientific carries Cole Parmer Glove Bags Handling of liquid pyrophorics must be conducted via cannula or syringe transfer to prevent exposure to air - if not manipulated within an inert atmosphere (see below for more details).

4.2 Manipulation of these reagents via syringe or cannula should always be conducted in a certified chemical fume hood, over a spill tray if possible, with the sash at the lowest practicable working height.

4.3 A blast shield should be positioned to protect against explosion.

4.4 Needles used for liquid transfer should be equipped with locking mechanisms to prevent accidental disconnection and release of reagents.

4.5 Mineral oil bubblers must be employed at all times to release excess pressure from reagent or reaction vessels that can contribute to accidents.

4.6 Balloons used for air-sensitive reagents are not suitable for use with pyrophorics.

4.7 Experiments with pyrophoric reagents should never be conducted without a second individual present.

5.0 TECHNIQUES FOR REAGENT TRANSFER

(Adapted from Sigma-Aldridge Technical Bulletins AL-134 and AL-164)

5.1 <u>Equipment Preparation</u>

Locate a needle of appropriate length and gauge. A sixteen-gauge needle is recommended if you plan to draw from the reagent container several times, as anything greater than this will leave a hole too large for the Teflon septum on the reagent bottle to reseal. A long needle is best if using a syringe. A long double-tipped flexible needle can be used for cannula transfer. Luer lock needles, or needles otherwise equipped with a locking mechanism, are highly recommended as a guard against the needles becoming detached.

Flush your syringe-needle assembly, if using one, with dry, high-quality inert gas such as nitrogen or argon before starting. Ensure that it is leak-free by inserting the needle into a rubber stopper. You should be able to compress the syringe to half its original volume without any leaks. The needle can be left in the rubber stopper when not in use to prevent the entry of air. Ensure that all glassware and other equipment involved in the procedure are clean and dry. Glassware should be heated in an oven to remove moisture, and cooled in an inert atmosphere.

Prepare an inert gas line for supplying positive pressure to the reagent container. Use a dry, high quality inert gas cylinder with a pressure regulator set to the lowest pressure sufficient for your work (no more than 5 psi), attached to flexible plastic tubing. A mineral oil bubbler should be added to the line, typically off of a manifold, to release excess pressure. A hypodermic needle at the end of the tubing can be used to insert the line through the septum of the reagent container. This needle can be inserted into a rubber stopper when not in use to prevent the entry of air.

The reaction vessel will also need to be supplied with a small amount of positive pressure during the reaction to prevent any pressure reversals that could cause air to enter the vessel. An inert gas line equipped with a mineral oil bubbler to relieve excess pressure will be needed for this. Run the reaction in a Schlenk flask that is under positive pressure from the inert gas line, connected via the tubing adapter. If the reaction vessel has a septum inlet, a hypodermic needle attached to the gas line can be pushed through the rubber septum to the reaction vessel, though the Schlenk vessel is better suited for controlling the atmosphere.

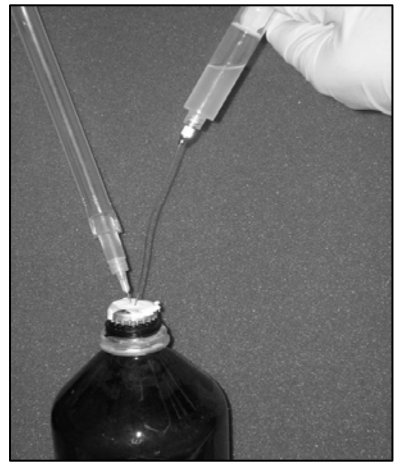
5.2 Syringe Transfer

Transfer of pyrophoric reagents via syringe is convenient, but should not be used for more than 50 mL. Clamp your reagent container firmly. You will need a small amount of positive pressure in the reagent container in order to draw the reagent into a syringe. Insert an inert gas line with low positive pressure (1-2 psi). Ensure that excess pressure is released through the mineral oil bubbler that is attached to the gas line. Simply sticking a needle through the septum, or using a balloon to relieve pressure, is **not** safe for pyrophoric reagents.

Prior to starting the procedure, ensure that the reaction vessel you plan to deposit your reagent into has a mineral oil bubbler to relieve pressure (if a bubbler is not already on the gas line), and that it is thoroughly flushed with inert gas prior to use. Again, do not use a balloon, and do not simply stick a needle through the septum to relieve pressure. Before beginning, set aside an Erlenmeyer flask with the same solvent in which your reagent is dissolved. If it is a neat reagent, use a solvent that is inert and unreactive towards that reagent. Aliquot slightly more than the volume you will be transferring with the syringe. This flask will need to be immediately available after the transfer for flushing out your syringe.

Draw slightly more than you need initially. Be careful to pull only very gently on the plunger as pulling too strongly can cause leaks and create air bubbles. Always keep a good grip on BOTH the needle and the plunger to ensure that neither comes off. If the plunger is ejected with its contents due to excess pressure, you will have a dangerous fire on your hands. (Fig. 1, next page – top right)

Fig. 1. Drawing reagent into syringe from reagent container, with inert gas line inserted.



Flip the syringe needle-up, so that the inert gas bubbles rise to the top (a long needle is needed for this). It is best to avoid allowing the reagent in the bottle to come into contact with the septum to prevent degradation. Tap the syringe a couple of times and look to make sure all the air/gas has been collected at the tip. (Fig. 2 – below left)

Push the plunger down to eject the inert gas and excess reagent back into the reagent vessel, stopping once the volume you need for your experiment is reached (Fig. 3 – below right).

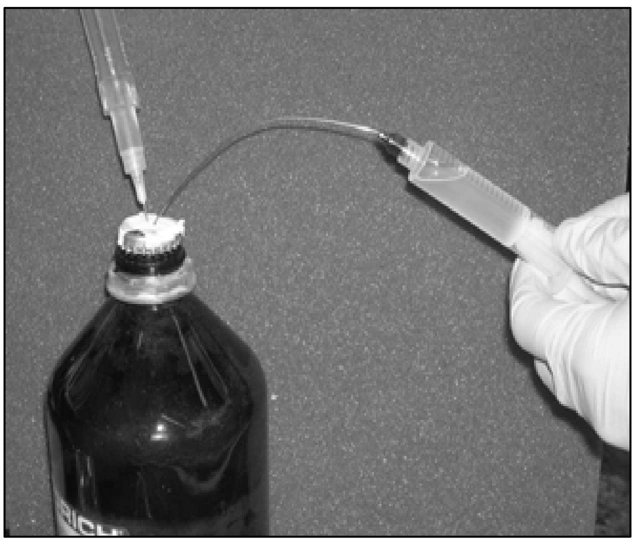


Fig. 2 Syringe is flipped needle-up after drawing liquid to allow inert gas bubbles to rise to needle.

Fig 3. Inert gas bubbles and excess liquid are forced back into reagent bottle.

Pull the needle into the headspace of the reagent bottle and draw a small amount of inert gas into the syringe. This prevents spilling, and very importantly protects the liquid from exposure to air during transfer. (Fig. 4, next page – top left)

Pull the needle into the headspace of the reagent bottle and draw a small amount of inert gas into the syringe. This prevents spilling, and very importantly protects the liquid from exposure to air during transfer. (Fig. 4) The needle can now be removed from the bottle, keeping the inert gas layer at the syringe tip. If you see a small flame at the tip of the needle, do not panic. You can use a beaker of sand to extinguish this. (Fig. 5, next page – top right)

Fig. 4 Needle tip is brought into headspace of bottle and an inert gas layer is drawn into syringe needle-up to prevent spilling

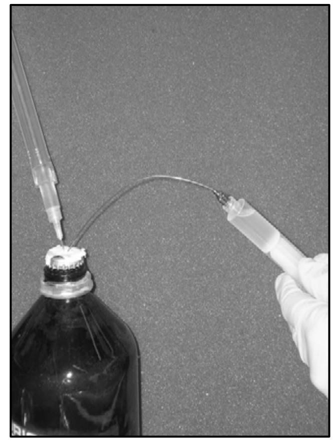


Fig. 5 Needle is carefully withdrawn from reagent bottle. Syringe is kept needle-up to prevent spilling

Insert the syringe into the septum of the reaction vessel, keeping the inert gas layer between the syringe and needle, if you have a long needle. Ensure that the vessel is equipped with an inert gas line to provide positive pressure, and a mineral oil bubbler to relieve excess pressure. Holding the plunger down, inject the inert gas cushion in your reaction first, and then inject your liquid into the flask.

5.3 Cannula/Double-Tipped Needle Transfer

Transfer of pyrophoric reagents via cannula is recommended for 50 mL or more. Clamp your reagent container firmly. You will need to create a small amount of positive pressure in the reagent container in order to force the reagent through your double-tipped needle. Connect it to an inert gas line to provide low positive pressure (1-2 psi). Ensure that the line is equipped with a mineral oil bubbler to relieve excess pressure. Using a balloon or simply sticking a needle through the septum to relieve pressure is **not** safe for pyrophoric reagents.

Make sure, before starting, that the reaction vessel into which you plan to deposit your reagent has a pressure release mechanism such as a mineral oil bubbler on the inert gas line, and that it is thoroughly flushed with inert gas prior to use. Again, do not use a balloon or simply stick a needle through the septum to relieve pressure.

Insert one end of the double-tipped needle into the headspace of the reagent vessel and allow the positive pressure from your inert gas line to flush the needle free of air. Insert the other end of the double-tipped needle through the septum of the reaction vessel. To allow for a measured transfer, you can use a sealed, measured funnel attached to the reaction flask, with the septum at the top of the funnel. When ready to transfer, push the needle that is in the headspace of the reagent container down into the liquid. The pressure from the inert gas line will begin forcing the liquid through the double-tipped needle.

When the desired volume has been transferred, pull the end of the needle in the reagent container up into the inert gas headspace and allow it to be flushed with inert gas again. Remove the end of the needle from the reaction flask first, and then from the reagent container. If, upon removal, a flame is lit at either tip, extinguish it in a beaker of sand.

5.4 Equipment Cleanup

If you use a syringe transfer, the syringe will have a small amount of the reagent remaining. Fill an Erlenmeyer flask with a small amount of the same solvent in which the reagent was stored, using slightly more than the volume which the syringe was used to transfer. If the syringe was used for a neat reagent, use a solvent that is inert and unreactive toward the reagent.

Ensure that any flame at the tip of the needle is extinguished first, and put the tip of the needle beneath the liquid in the flask, keeping it beneath the solvent. Carefully draw the solvent into the syringe and eject it to flush the syringe, and repeat for a total of three rinses. Afterwards, the syringe can be disposed of by putting it into a sharps container, if it is disposable. The solvent in the flask, with trace amounts of the pyrophoric compound, should be added to your solvent waste container. Be sure to list all of the components on the chemical/hazardous waste label.

For a cannula transfer, the double-tipped needle should have been purged with inert gas before you removed it. The needle can be place in a sink in the absence of any solvents or other combustible materials. Flush the needle with water, collecting the effluent for disposal with your aqueous waste. Making sure that there is no longer any reactivity; use a wash bottle to flush the needle with acetone, collecting the effluent with your solvent waste.

6.0 STORING PYROPHORIC REAGENTS

6.1 Pyrophoric liquids, or compounds dissolved in a liquid, should be stored in sealed containers with PTFE-lined septa to prevent air exposure.

6.2 Pyrophoric materials must be used and stored away from all other flammable and combustible materials such as paper, bench liners, and solvents. Even open containers of water should be kept away due to the potential for a violent reaction.

6.3 Reagent bottles typically come in secondary containment within metal cans. Keep the manufacturer's can for reagent storage and for disposal of the bottle after completion of the experiment involving the material.

7.0 DISPOSAL

7.1 For any significant amount of reagent remaining in the reagent bottle, first ensure that the bottle is purged with inert gas. Purge a secondary container such as the manufacturer's can in which the bottle was shipped, with an inert atmosphere. Put the reagent bottle into this purged secondary container and seal, then complete a chemical/hazardous waste label and submit an online chemical waste pickup request at http://eohwprod.umdnj.edu/eohss3.cfm

7.2 If only trace amounts of the reagent remain in the reaction flask or original bottle, use the solvent in which the reagent was originally stored to triple rinse the bottle (under positive pressure from an inert gas line when purging), collecting the rinse in a separate container. Place the solution in a properly labeled separate solvent waste container.

7.3 To dispose of a bottle containing a significant quantity of unused reagent seal it inside a secondary container, such as the metal can that came with the reagent which has been purged with inert gas. Complete the chemical/hazardous waste label and submit an online pickup request.

8.0 PERSONAL PROTECTIVE EQUIPMENT

8.1 When conducting experiments and handling pyrophoric or highly reactive reagents, personnel must wear lab coats made of flame resistant materials such as DuPont Nomex. The lab coat should be worn in such a fashion that personal clothing is completely covered (a key word search on the term "flame resistant lab coats" will provide information on sources). Legs should be covered below the lab coat with long pants. Avoid synthetic fibers such as polyethylene, PVC, nylon etc. Synthetic polymers typically melt and stick to the skin during a fire. Alternatively, full body coveralls made of fire resistant material can be worn.

8.2 Gloves made of Nomex or other fire resistant material must be worn. Double gloving with an interior polymer glove may be included if the experimental protocol presents a risk of significant spilling and saturation of the outer glove.

8.3 Open toed shoes are prohibited along with sneakers or canvas shoes that can ignite more readily.

8.4 Fully enclosed safety goggles or a face shield are preferred, if available, as they offer greater facial protection than safety glasses.

8.5 Tie back all loose hair to prevent ignition in the event of a flash fire.

9.0 EMERGENCY PREPAREDNESS AND RESPONSE

9.1 Locate experiments in hoods closest to safety showers.

9.2 Test the eyewash before beginning experiments.

9.3 Keep the areas around the eyewash and shower clear from obstruction at all times.

9.4 Keep a container of soda ash or sand within arm's reach in case a small fire occurs, as this can be safely used to smother the flames. Users may encounter small fires at the tips of needles – know to expect this, and do not panic if you see it. A beaker of sand is useful for extinguishing this "pilot light".

9.5 **DO NOT** use a class "ABC" or CO_2 fire extinguisher to attempt to quench a fire involving pyrophoric reagents – this can greatly exacerbate the problem. A class "D" fire extinguisher must be used for large quantities of pyrophorics. Personnel should be familiar with how to use this piece of equipment.

9.6 For skin exposures, rinse with water for 15 minutes; immediately notify Public Safety that first aid is needed: Newark Campus - 2-4490 or 222; Piscataway and New Brunswick Campuses - 5-4000; Stratford and Camden Campuses - 7-7777**).**

10.0 TRAINING

10.1 All laboratory staff members who work in the room, even if not working directly with pyrophoric/highly reactive chemicals, should receive training regarding the hazards of pyrophoric chemicals and emergency actions. All training should be documented by filling out the signature sheet at the end of this document.

10.2 All laboratory staff members who work in the room should also review the location of the eye wash, safety shower, class "D" fire extinguisher, any additional extinguishing media (e.g., sand), the fire alarm pull station, emergency gas shutoff, and chemical spill cleanup kits.

10.3 Staff who work directly with the pyrophoric or highly reactive reagents should be given hands-on training on laboratory techniques and the proper use of all equipment designed to prevent exposure (e.g., chemical hoods, glove boxes, etc.) . The written SOP should also be discussed and reviewed by these staff members

11.0 SOURCES AND REFERENCES

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Photos provided by Uttam Tambar, Columbia University

STANDARD OPERATING PROCEDURE
for
WORKING with PYROPHORIC CHEMICALS

TRAINING SHEET

Date	Print Name	Signature

INSTRUCTOR: Describe the training session. Provide as much specific information as possible (e.g., demonstration of emergency equipment, hands-on demonstration, review of SOP): ______________________________

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Name: _____________________ **Signature:** ______________________________

Date: __________________ **Job Title:** ____________________________________