UMassAmherst
The Commonwealth's Flagship Campus

Environmental Health & Safety
Draper Hall, 40 Campus Center Way
Amherst, MA 01003
Tel: 413-545-2682

PYROPHORIC LIQUIDS & SOLIDS **Standard Operating Procedure**	**Document Number: EHS-AS-100** **Effective Date: 2/8/18** **Revision Date: 2/8/18**

1.0 Purpose and Applicability

1.1 The purpose of this policy is to ensure the proper management of liquid and solid pyrophoric compounds in order to reduce uncontrolled reactions and fires. Pyrophoric compounds can also exist as gases and will be addressed separately. The use of pyrophoric gases will require approval of the Institutional Chemical Safety Committee (ICSC).

1.2 This policy applies to all personnel who handle pyrophoric liquid compounds on the University of Massachusetts Amherst campus and its research stations.

1.3 It is expected that all users of pyrophoric materials will:

1. Never work alone with them
2. Have direct training and over sight by the Principal Investigator (PI) and follow a written procedure
3. Keep work area neat, clean and free of combustible materials
4. Wear appropriate personal protective equipment (PPE) including flame retardant lab coat, inner nitrile gloves with outer flame retardant gloves (if required by the PI), safety goggles, and face shield (as required)
5. Verify safety equipment (fume hood, fire extinguisher, drench shower, eye wash) is available and functional by checking certification tags
6. Conduct all experiments in a fume hood or glovebox

2.0 Definitions

2.1 What is a pyrophoric material?

A material with the ability to **spontaneously ignite**, without the influence of heat or fire, in air at temperatures of 130^{o} F (54^{o}C) or below. They can be in the solid, liquid or gas phase. Pyrophoric gases, liquids, and solids all share the property of spontaneous ignition in contact with air. Pyrophoric liquids such as tert-butyllithium are often metal- (alkyls, aryls, vinyls, carbonyls or hydrides) complex solutions in flammable solvents such as THF, ether, pentane or heptane, however, some are available as neat liquids as well. Pyrophoric solids such as lithium are often alkali metals and stored under kerosene or oil. Additional chemical and physical properties of pyrophoric compounds could include:

- Corrosive
- Water reactive
- Peroxide forming
- Solid, liquid and gaseous forms

3.0 Roles and Responsibilities

3.1 Key Personnel—Principle Investigator and personnel under his/her supervision. The Principle Investigator is responsible for training his/her students and staff in the proper handling of pyrophoric compounds and the use of personal protective equipment, and for documenting this training. Lab personnel must identify additional hazards specific to the pyrophoric chemicals they are working with by a review of the appropriate Safety Data Sheets prior to commencing lab work. This hazard review should be documented. All laboratory safety training required by EH&S must be up-to-date including Fire Safety Training with hands on practice using fire extinguishers.

3.2 Environmental Health and Safety (EH&S) – Is responsible for maintaining an inventory of pyrophoric materials, inspecting the labs where they are used, providing general lab and fire safety training, providing emergency response and assisting with spill clean-up..

4.0 Procedure

4.1 **Engineering Controls and Personal Protection**

4.1.1 **Storage**

Pyrophoric compounds should be stored and handled in areas free of ignition sources, and containers should be stored under an inert atmosphere. Gloveboxes may be used to provide the inert atmosphere.

Equipment:

Needles, syringes and other utensils used with pyrophoric reagents must be cleaned immediately after use to avoid clogging the needles and seizing the syringes.

1. Draw hexane into the syringe containing small amounts of pyrophoric reagent and then discharge the diluted solution into isopropanol.
2. Similarly, flush cannulae (i.e., double-tipped needles) with hexane and then quench hexane wash in isopropanol.

Glassware preparation:

Laboratory glassware contains a thin film of adsorbed moisture which can be removed by heating in an oven (125 °C/overnight or 140 °C/4 hrs). The hot glassware should be cooled in an inert atmosphere by assembling the glassware while hot and flushing with a stream of dry nitrogen or argon. A thin film of silicone or hydrocarbon grease must be used on all standard taper joints to prevent seizure upon cooling. Alternatively, the apparatus may be assembled cold and then warmed with a heat gun while flushing with dry nitrogen. The oven-drying procedure is more efficient than using a heat gun because it removes moisture from inner surfaces of condensers and from other intricate parts.

4.1.2 **Designated Areas**

Experimental areas involving pyrophoric compounds should be confined to a designated fume hood in the laboratory. This area should be recognized by everyone in the laboratory as a place where special precautions, laboratory skill, and safety discipline are required. Post signs conspicuously to indicate designated areas and responsible parties to contact in case of emergency.

4.1.3 **Eye Protection**

Always wear chemical splash goggles. Safety goggles must have ANSI z87+ certification. Work with the hood sash as low as feasible or work within a glovebox for added protection. A blast shield may also be necessary for certain types of experiments.

4.1.4 **Body Protection**

A properly fitted FRC rated lab coat is required. Sleeves must be at the correct length and not rolled up. No open-toed shoes or shorts in the lab. Leather shoes (not fabric or mesh) should be worn.

4.1.5 **Gloves**

Appropriate gloves with a minimum thickness of 0.4 mm extended up the wrist is recommended. In addition, flame retardant outer gloves may be required.

4.2 **Safety Precautions For Handling And Storage**

4.2.1 **Safe Work Practices**

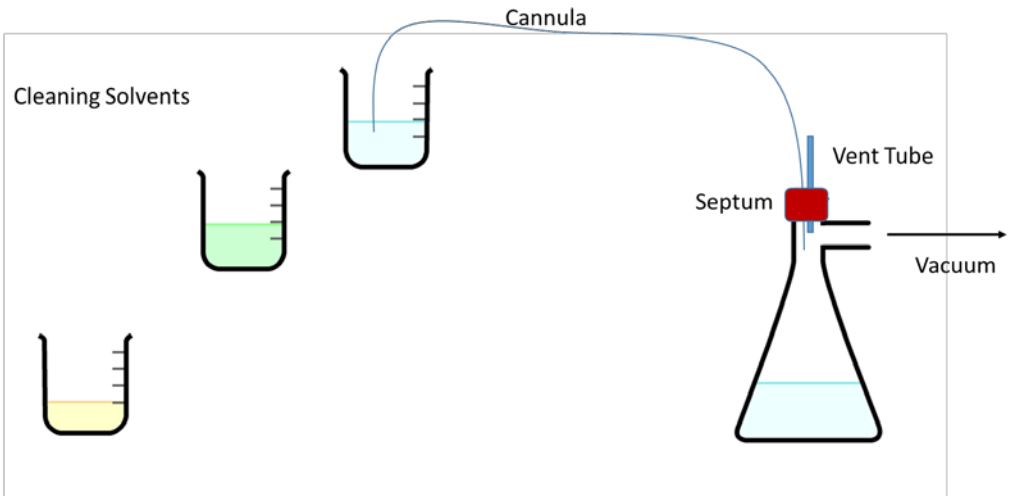
Do not eat, smoke, or drink where pyrophoric compounds are handled because in addition to the flash hazard many are also toxic. Wash hands thoroughly after handling. Areas of work with pyrophorics should be clearly defined and labeled, and decontaminated regularly. All extraneous combustible and flammable materials must be removed from the hood and work area. A written protocol must be provided by the PI responsible for the laboratory before handling pyrophoric compounds. It is a good idea to perform a "dry" run of the procedure with only solvent to ensure comfort with Schlenk and air-free techniques particularly for inexperienced lab personnel. Dispensing equipment must be clean and verified as suitable for use with pyrophoric compounds. Adequate quenching gas must be available and in use. Review the Safety Data Sheet (SDS) prior to use of any pyrophoric compound. Verify that fire suppression materials are present and that the emergency eyewash unit is flushed and functioning.

Transferring Pyrophoric Reagents with a Cannula

A 20 minute safety video on Handling Pyrophoric Materials is available as a supplement to hands on training by the PI (https://www.youtube.com/watch?v=iLMl10X0Naw). Note cannula cleaning procedure should be carried out as described below rather than as shown in the video.

Cleaning procedure for cannulae

An apparatus such as that shown below should be used to clean all cannulae. The vent tube can be covered or uncovered with a gloved finger to control suction. Alternatively, a piece of pliable tubing with a hose clamp can be used for this purpose.



Transferring Pyrophoric Reagents with Syringe

- Clamp the reagent bottle and receiving vessel to prevent them from moving.
- Insert a needle from an inert gas source with a bubbler outlet into the reagent bottle keeping the needle tip above the liquid level.

-NOTE: The goal of this technique is to equalize the pressure in the reagent bottle.

- Flush dry syringe several times with inert gas from a separate purged vessel, depress the plunger and insert the needle into the Sure/Seal bottle.

-NOTE: For large volume syringes, use a corresponding larger gauge needle.

- Gently pull the plunger to draw liquid into the syringe. Pulling too hard or too fast can cause air bubbles to enter between the plunger and syringe body.

-NOTE: Simple glass syringes are more prone to causing gas bubbles.

- Disposable plastic syringes have a good seal on the plunger and work well, however, be careful to not seize the syringe. This can happen if the rubber end of the plunger swells because it is in contact with the reagent for too long of a time. Glass syringes with Teflon-tipped plungers (gastight) syringes are best and recommended. For safest work, do not fill syringe more than 60% full, up to a maximum of 10 mL of liquid. The cannula (double-tipped needle) technique is safer when transferring 10 mL or more.
- FOR HIGHLY PYROPHORIC materials such as *tert*-butyllithium and trimethylaluminum, it is best to draw a plug of inert gas from the headspace into the needle after excess reagent is forced back into the bottle and before withdrawing the needle.
- The desired volume of reagent in the syringe is quickly transferred to the reaction apparatus by puncturing a rubber septum
- The syringe and needle should then be washed with hexanes and the washes quenched in isopropanol as described above. More than incidental amounts of residual pyrophoric materials may require a more thorough quenching process involving progressive reaction with more protic alcohols, and possibly water and acid (e.g., isopropanol quench followed by ethanol, then methanol, then water, then dilute acid).

Engineering Controls

The following is a general plan for all pyrophoric materials:

1. Work under an inert atmosphere (e.g., argon, nitrogen) in a glove box, vacuum manifold or any enclosed inert environment inside a fume hood.
2. Keep the material under inert atmosphere (e.g., nitrogen, argon) when not in use.
3. Only when absolutely necessary to transfer larger quantities of pyrophorics, use an appropriately-designed, engineered system that is tested and properly used.

4.2.2 **Emergency/First Aid Procedures for Pyrophorics**

4.2.2.1 The primary risk is spontaneous fires caused by contact with air or moisture. **Should a fire occur, no matter how small, pull the fire alarm before attempting to extinguish the fire.** Extinguish flames using a non-reactive media. Acceptable fire extinguishing media include Met-L-X, soda ash (lime) or *dry* sand to respond to small fires, and an ABC extinguisher for large fires. The extinguishing media should be located near where the pyrophoric work is occurring. **DO NOT use water** to attempt to extinguish a pyrophoric/reactive material fire as it can enhance the combustion of some of these materials, e.g. metal compounds, and do not use water or CO_2 extinguishers on an organolithium fire. A small beaker of Metal X/LithX, dry sand or soda ash (lime) in the work area is useful to extinguish any small fire that occurs at the syringe tip and to receive any last drops of reagent from the syringe. In general, an ABC dry powder extinguisher will put out the fire, but the pyrophoric reagent may reignite. You may only attempt to extinguish small fires if ALL of the following conditions apply: (1) the fire alarm has been activated, (2) you have been trained to use a fire extinguisher, and (3) it is safe for you to attempt to extinguish the fire. Otherwise, (1) close the door the lab to contain the fire, (2) proceed to the nearest exit (use stairs, not the elevator), (3) pull the fire alarm, (4) evacuate the building and assemble in your designated area for a head count.

Skin Contact: Move to the safety shower or other water source and flush the contaminated skin using soap or mild detergent and water for at least 15 minutes. For more than incidental exposure, have someone call 911 (or 5-3111 from a campus line, or 413-545-3111 from a cell phone) to request medical assistance. Report the identity of the materials involved, and provide SDSs to the first responders if possible.

Eye Contact: Immediately flush eyes with large amounts of water for at least 15 minutes, lifting lower and upper lids occasionally. Have someone call 911 (or 5-3111 from a campus line, or 413-545-3111) to request medical assistance. Report the identity of the materials involved, and provide SDSs to the first responders if possible.

Inhalation of Vapors: Immediately move victim to fresh air and get medical attention. Keep victim warm, quiet, and comfortable. If breathing has stopped, perform cardiopulmonary resuscitation. Make sure mouth and throat are free of foreign material. For more than incidental exposures, have someone call 911 (or 5-3111 from a campus line, or 413-545-3111) to request medical assistance. Report the identity of the materials involved, and provide the SDSs to the first responders if possible.

Report any spill, skin or eye contact, or inhalation of vapors to EH&S as soon as possible by calling 413-545-2682 and submit a lab incident report form. Report all fires to 911.

4.2.3 **Examples of Pyrophoric Reagents**

Alkylaluminum reagents (Neat or in hydrocarbon solvents) (Neat reagents are VERY pyrophoric)
Alkyllithium reagents (Typically in hydrocarbon solvents) (*Tert*-butyllithium is VERY pyrophoric)

Alkenyllithium and Aryllithium reagents (Typically in hydrocarbon solvents)
Alkynyllithium reagents (Typically in hydrocarbon solvents)
Alkylzinc reagents (Neat reagents are pyrophoric)
Boranes (Neat reagents are pyrophoric)
Grignard Reagents (RMgX) (Typically in hydrocarbon solvents)
Lithium Aluminum Hydride 95 %
Potassium hydride, dispersion in mineral oil
Sodium Cyanoborohydride
Sodium Hydride (neat solid, or can be in mineral oil)
Trimethylaluminum
Trimethylgallium
Tri- t-butylphosphine, 99% (Assay)

4.2.4 Fire Protection

Fire Extinguishers are ***required****. Contact EHS for advice selecting extinguishers or to receive training.*

☐Do NOT use Extinguishers containing or developing water, carbon dioxide or halons. They are not suitable for firefighting organolithium compounds as they react violently.

- Class A, B, C (dry chemical) for pyrophoric liquids and supporting flammable solvents
- Class D (recommended for certain materials) such as reactive metals
- Keep a container of Powdered lime (CaO, calcium oxide), Soda Ash (Na_2CO_3) or Sand (SiO_2), or Met-L-X within arm's length when working. Containers of extinguishing media should have secure covers. Media should be checked regularly for moisture buildup, which will cause clumping of the material.

4.2.5 **Pyrophoric Waste**

4.2.5.1 **Dispose of Waste**

- Dispose of regularly generated chemical waste within 6 months
- Call EH&S for questions
- Empty Containers
    - Dispose as hazardous (irrespective of the container size)
    - Any container with a residue of reactive materials should never be left open to the atmosphere.
    - Any unused or unwanted reactive materials must be destroyed by transferring the materials to an appropriate reaction flask for hydrolysis and/or neutralization with adequate cooling. More than incidental amounts of residual pyrophoric materials may require a more thorough quenching process involving progressive reaction with more protic alcohols, and possibly water and acid (i.e., isopropanol quench followed by ethanol, then methanol, then water, then dilute acid).
    - The empty container should be rinsed three times with an inert dry COMPATIBLE solvent; this rinse solvent must also be neutralized or hydrolyzed. The rinse solvent must be added to and removed from the container under an inert atmosphere.
    - After the container is triple-rinsed, it should be left open in back of a hood or ambient atmosphere at a safe location for at least a week.

- The empty container, solvent rinses and water rinse should be disposed as hazardous waste and should not be mixed with incompatible waste streams

4.2.5.2 **Disposal of Pyrophoric or Water Reactive Contaminated Materials**

• All materials – disposable gloves, wipers, bench paper, etc. - that are contaminated with pyrophoric chemicals should be disposed as hazardous waste.

• The contaminated waste should not be left overnight in the open laboratory but must be properly contained to prevent fires.

5.0 Key References

1. Sigma-Aldrich Technical Bulletins AL-134, AL-164
2. Pacific Northwest National Laboratory, PNNL 18668
3. Dartmouth College Training video on "Handling Pyrophoric Materials" https://www.youtube.com/watch?v=iLMl10X0Naw