UMassAmherst | Environmental Health & Safety

Pyrophoric Liquids and Solids SOP

Summary

- Pyrophoric materials have the ability to spontaneously ignite without influence of heat or fire at low temperatures, so they must be properly handled to minimize this risk.
- Experiments involving these materials should be confined to a designated space in the lab where all members are aware of the heightened risk.
- Appropriate handling and PPE should be used as outlined in this SOP

What are pyrophoric materials?

A material with the ability to **spontaneously ignite**, without the influence of heat or fire, in air at temperatures of 130° F (54°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

Some examples of pyrophoric compounds include:

- 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)

What are the hazards?

Pyrophoric materials carry an inherent fire hazard and burn risk to the user. Along with the fire hazards, some of the chemicals can also be corrosive or peroxide forming. 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. The three GHS indicators above are not a comprehensive list of the hazards associated with every pyrophoric compound used, but are three more common indicators found along with these chemicals.

What activities could pose a risk?

When handling pyrophoric compounds, there are many times that risk could be involved. When transferring the material, there is spill risk. If there is residual compound left during the cleaning process, combustion could occur. To minimize risk, follow the procedures outlined in this SOP.

General considerations

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

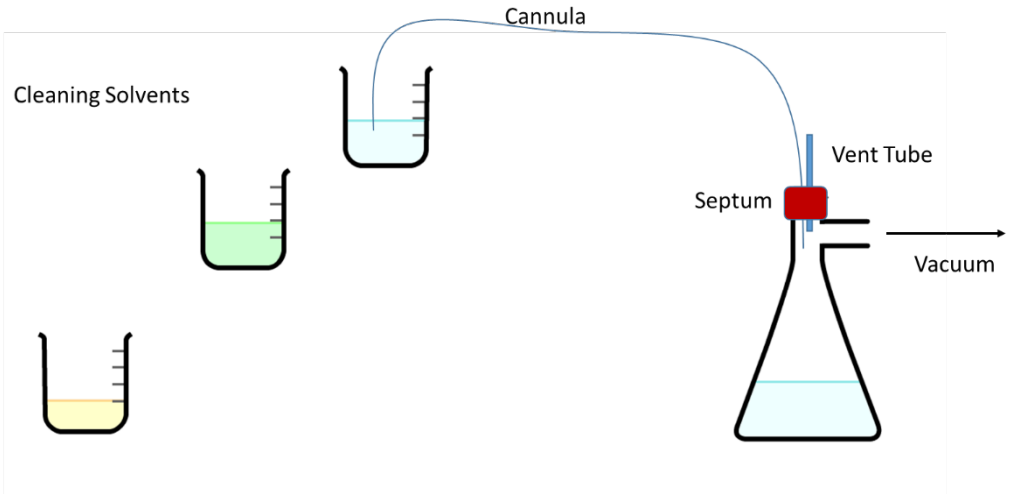
to use of any pyrophoric compound. Verify that fire suppression materials are present and that the emergency eyewash unit is flushed and functioning.

Transferring 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 cannulas

An apparatus such as that shown below should be used to clean all cannulas. 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 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.

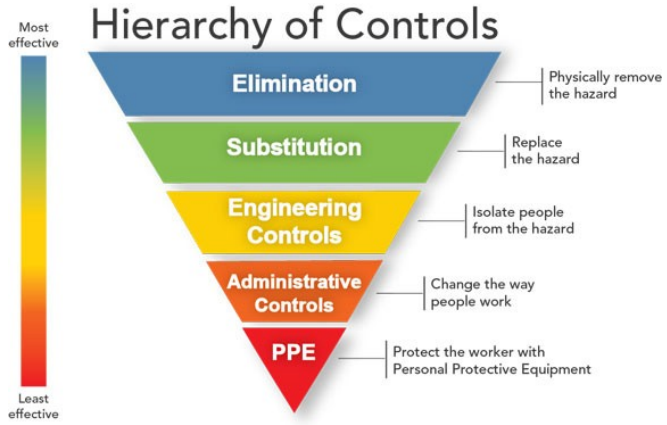
- Gently pull the plunger to draw liquid into the syringe. Pulling too hard or too fast can cause air bubbles to enter between the plunger and syringe body.

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).

How can exposures be minimized?

As with any other hazardous material, always conduct a thorough risk assessment and employ the hierarchy of controls to minimize risk when working with pyrophoric compounds. Some specific applications of the hierarchy of controls to these hazards are listed below.



Always apply the controls in the order of most effective to least effective (see graphic), and apply as many controls as possible to reduce the risk to the lowest achievable level.

Elimination/Substitution

- Only use a pyrophoric compound when absolutely necessary. Parse the literature and talk with your lab members/PI before deciding you need to use these materials. If a lower hazard alternative exists, try that first.

Engineering Controls

The following is a general plan for all pyrophoric materials:

- Work under an inert atmosphere (e.g., argon, nitrogen) in a glove box, vacuum manifold or any enclosed inert environment inside a fume hood.

- Keep the material under inert atmosphere (e.g., nitrogen, argon) when not in use.
- Only when absolutely necessary to transfer larger quantities of pyrophorics, use an appropriately-designed, engineered system that is tested and properly used.

Administrative Controls

- Before use:
    - Consult the manufacturer's Safety Data Sheet and additional chemical information at https://cems.unh.edu/umass/CEMS/SearchSDS
    - Locate nearest eyewash and shower and confirm that they are accessible and within 50 ft. of the work area.
    - Make sure all equipment is in working order for the material about to be used:

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.

- As mentioned previously, keep these materials in designated places in the lab. This ensures that all laboratory personnel recognize this space requires special precautions. Post signs to indicate this area and ensure sign has contact information for responsible party in case of emergency.

Personal Protective Equipment

- Always wear proper PPE when handling pyrophoric compounds including:
    - Wear chemical splash goggles with ANSI z87+ certification. A blast shield may also be necessary for certain experiments.
    - A properly fitted FR rated lab coat is required. Sleeves must be at the correct length and not rolled up.
    - Closed toed shoes and long pants required, tie back long hair.
    - 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.

Waste Handling

- 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

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.

Exposure and Spill Procedures

Report any spill, skin or eye contact, or inhalation of vaports to EH&S as soon as possible by calling 413-545-2682 and submit a lab incident form. Call 911 for fire reporting.

Fire protection

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.

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.

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.

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