1 Introduction

This document offers a short and concise overview of reactive materials. Understanding the following content is a crucial prerequisite in understanding basic safety fundamentals such as 1) hazard awareness, 2) engineering controls, 3) work practices, 4) PPE and 5) emergency response for working with reactive materials.

2 Scope

The guideline applies to lab personnel, and it has been developed to assist them in the preparation of lab specific SOPs.

3 Procedure

3.1 Introduction to Reactive materials

Pyrophoric and water reactive materials can ignite spontaneously on contact with oxygen in the air, moisture in the air or water. Failure to follow proper handling procedures can result in fire or explosion, leading to serious injuries, significant damage to facilities and/or death. This document describes the hazards, proper handling, disposal and emergency procedures for working with pyrophoric, water reactive and moisture sensitive materials.

Any handling of a pyrophoric or water reactive material is high risk and must be controlled with adequate experimental design, direct supervision and training. These tasks require two people and should not be performed alone.

Researchers should prepare and/or review written standard operating procedures (SOP) before working with such reactive reagents. The written SOP must include information on how to do the work safely. The safety information in this document can assist with the development of an SOP specific to the laboratory procedure.

Examples of Pyrophoric/Water Reactive Materials are:

- Metal alkyls and aryl compounds: diethyl zinc, dimethyl cadmium, trimethyl aluminum
- Alkyl lithium or organolithium compounds: *tert*-butyllithium, *sec*-butyllithium, *n*-butyllithium, methyl lithium.
- Grignard Reagents: RMgX (R=alkyl, X=halogen), methylmagnesium bromide
- Metal carbonyls: nickel tetracarbonyl
- Metal powders (finely divided): Cobalt, iron, zinc, zirconium, barium strontium, calcium, hafnium
- Metal hydrides: Sodium hydride, lithium aluminum hydride; Nonmetal hydrides: Diethylarsine, diethylphosphine
- Non-metal alkyls: R_3B, R_3P, R_3As; tetramethyl silane, tributyl phosphine
- White and red phosphorus
- Group I (Alkali) metals: Lithium, potassium, sodium, sodium-potassium alloy (NaK), rubidium, cesium

3.1.1 Hazards

Because these reagents react on contact with air and/or water, they must be handled under an inert atmosphere and in such a way that rigorously excludes air/moisture. Many come dissolved or immersed in a flammable solvent that may be hazardous. Besides extreme flammability, most of these materials are toxic and may cause damage to the liver, kidneys, and central nervous system.

3.1.2 Controlling the Hazards

BEFORE working with pyrophoric or water reactive reagents, read the relevant SOP, Safety Data Sheets (SDS), technical bulletins, and guidance documents to understand how to mitigate the hazards. The SDS must be reviewed before using an unfamiliar chemical and periodically as a reminder. Users of reactive materials must be trained in proper lab technique and be able to demonstrate proficiency. Do not work alone or during off hours, when there are few people around to help. The first few times you handle pyrophoric materials, seek more experienced researchers to show you proper technique and always let others in the lab know you will be working with pyrophoric materials. ALWAYS wear proper personal protective equipment.

Remove all excess and nonessential chemicals and equipment from the fume hood or glove box where pyrophoric or water reactive chemicals will be used. This will minimize the fuel if a fire should occur. Keep combustible materials, including paper towels and Kimwipes, away from reactive reagents.

Minimize the storage of pyrophoric or water reactive materials in your lab by ordering the smallest practical amount; handle and use the smallest practical quantity. It is safer to do multiple transfers of small volumes than to attempt to handle larger quantities at once. Alternatively, an appropriately engineered system, capable of safely transferring the larger quantity must be designed, tested and properly used.

3.1.3 Personal Protective Equipment

Eye Protection

- A full face shield must be worn over safety eyewear whenever handling pyrophoric chemicals unless protected by glove box or sash of the fume hood sash. Use combination sash and work behind it like a blast shield. Prescription eyeglasses, safety glasses, and splash goggles will not provide adequate protection of the face.
- All manipulations of pyrophoric chemicals which pose the risk of explosion, splash hazard, or a highly exothermic reaction must be carried out in a glove box or in a fume hood with the sash providing shielding.

Skin Protection

- A lab coat made of natural fibers or fire retardant material must be worn. Fire-resistant lab coats made from Nomex or other fire resistant materials are recommended. They need to be buttoned and fit properly so as to cover as much skin as possible. Clothing, shirt and long pants should be cotton or wool. ***Synthetic clothing is strongly discouraged*** *when working with pyrophorics.*
- In general, chemical protective gloves are not fully protective when working with pyrophorics. If the reactive material were to spill onto the gloved hand and ignite, nitrile or latex gloves would also ignite and contribute to a serious burn injury.
- A Nomex or leather flight glove (used by pilots to protect from heat and flash) will provide flash burn protection, but will not be chemically protective. A chemically protective glove can be worn

under the fire resistive gloves, because the reusable fire protective glove may become chemically contaminated.

- Appropriate shoes that cover the entire foot must be worn (closed toe, closed heel, no holes in the top). Long pants or skirts must be worn to protect the lower leg.
- If the clothing becomes chemically contaminated, it must be removed immediately and the skin must be thoroughly cleaned with soap and water. Dress in clean clothes after ensuring the skin is decontaminated.

3.2 Safety Equipment

Prior to starting activities with reactive compounds, researchers must have the proper safety equipment and emergency phone numbers readily available. Acceptable fire extinguishing media include Metal X, Class D fire extinguisher, 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. Prior to use, review the SDS for the proper fire extinguisher to use with the given material. In general, an ABC dry powder extinguisher will put out the fire, but the pyrophoric reagent may reignite. Class D fire extinguishers will put out fires of pyrophorics.

Eyewash/Safety Shower

- A combination eyewash/safety shower must be within 10 seconds of travel time from where reactive chemicals are used. Inside the laboratory is optimal.
- If your clothing should catch on fire, the deluge of water from the emergency shower will put out the fire. It is recommended to use the emergency shower even though water reactive materials may have been spilled.
- Before working with reactive reagents, verify that there is clear access to the emergency eyewash and safety shower. Flush the eyewash to verify that the equipment is working properly.
- It is helpful to have a robe, lab coat, or change of clothes near the safety shower to deal with modesty issues.
- Know what to do before the accident occurs. If you spill a pyrophoric liquid on you, ***DON'T PANIC,*** take off your contaminated lab coat and use the safety shower.

Fume Hood

- Many reactive chemicals release noxious or flammable gases upon decomposition and should be handled in a laboratory fume hood. In addition, some pyrophoric materials are stored under kerosene (or other flammable solvent); therefore, the use of a fume hood (or glove box) is required to prevent the release of flammable vapors into the laboratory.
- The fume hood sash should be used to provide shielding.
- Always work more than six (6) inches in from the front of the fume hood, to capture any fugitive vapors.

- Remove flammable and combustible materials from the area where pyrophoric materials are to be handled. For instance, flammable waste should not be stored in the hood where pyrophoric liquid will be handled.
- The fume hood should have a supply of an inert gas such as nitrogen or argon (with low moisture and oxygen content) for use with the experiment.

Glove (dry) box

- Inert atmosphere glove boxes are excellent devices for the safe handling of reactive materials. Glove boxes used for this purpose should be in good working order and the moisture and oxygen levels of the atmosphere should be confirmed prior to the introduction of reactive compounds into the box. Continuous monitoring of oxygen and moisture is highly recommended. Also, take into account interactions between items in the glovebox (e.g., nitrogen is not an inert gas for lithium metal as the lithium is reduced violently to lithium nitride).
- Before removing reactive materials from the glovebox, review the proper steps necessary to protect the material from air, or quench excess material before exposing it to air.

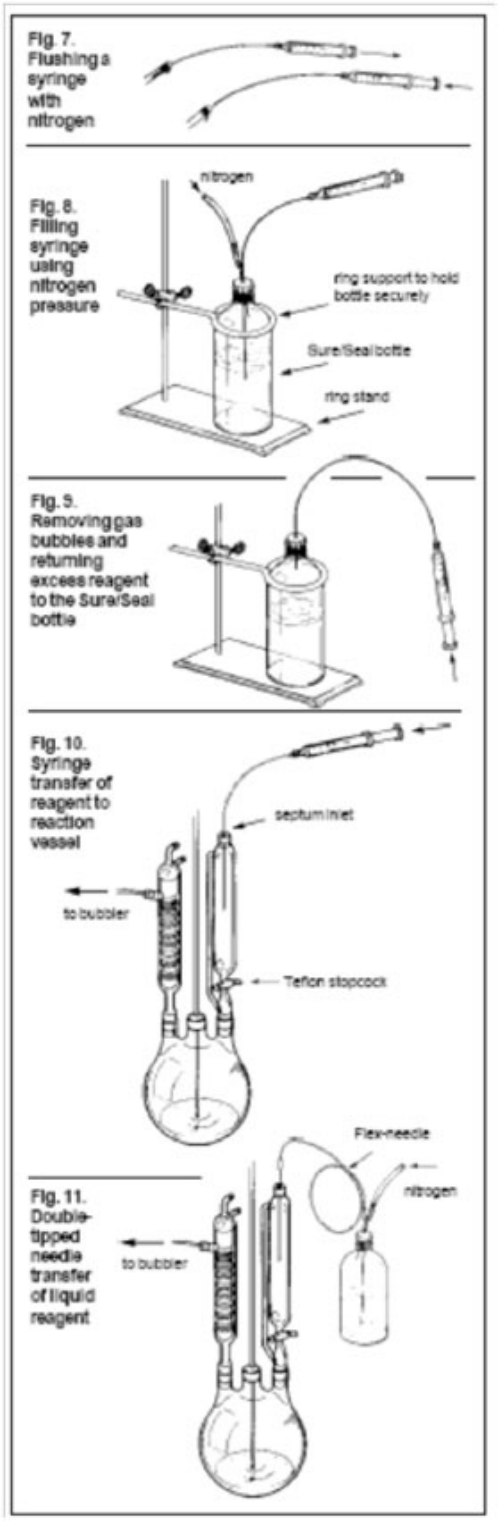
3.3 Important Handling Precautions

Reactive reagents can be handled and stored safely as long as all exposure to atmospheric oxygen and moisture or other incompatible chemicals is avoided. Finely divided solids can be transferred under an inert atmosphere in a glove box. Liquids may be safely transferred without the use of a glove box by employing techniques and equipment discussed in the *Aldrich Technical Information Bulletin AL-134 & 164*. Other good references include “Manipulation of Air–sensitive Compounds” by Shriver and Drezdzon and “Safe handling of organolithium compounds in the laboratory” Journal of Chemical Health and Safety, American Chemical Society, May/June 2002.

Handling Pyrophoric Liquids

- There are two basic techniques to transfer pyrophoric liquids: the syringe and the cannula needle. The syringe is normally preferred for small quantities (i.e. less than 20 mls)..
- Users should read and understand the Aldrich Technical Information Bulletin; there are many important steps that are not in this document. The research group should also have in place a laboratory-specific SOP for their specific procedures.
- By using proper syringe techniques, these reagents can be handled safely in the laboratory. A Schlenk line in a fume hood with inert gas flow will be necessary. The Aldrich Sure/Seal™ Packaging System provides a convenient method for storing and dispensing air-sensitive reagents.
- The reagent can be dispensed using a syringe (small quantity) or double-tipped needle (cannula method for large quantities). The needle should be no larger than 16 gauge, inserted through the hole in the metal cap, as shown in Fig. 9 below. It is recommended that the plastic cap be replaced after each use and, in particular, for long-term storage.
- Most researchers only need to use small quantities, so the syringe method works best. Be cautious with the use of the plastic syringe as the rubber gasket may swell up leaving you with a syringe of pyrophoric liquid. Start with small quantities, until you are proficient with the method.
- For extended storage of unused reagents, use the solid plastic cap, or equip the bottle with an Oxford Sure/Seal valve cap, or transfer the reagent to a suitable storage vessel, as described in the technical bulletin.

Be very careful when transferring pyrophoric liquids. If the syringe is pulled too hard, the pyrophoric liquid can come out the back of the syringe onto the researcher. Orient the syringe in such a way that an accidental spill will be directed away from you. The Aldrich method recommends using the plastic syringes only once, especially for larger syringes where the plunger may expand. Never overfill the syringe; fill the syringe half full, even if you need to make multiple transfers. Some individuals feel that the cannula method is much safer, even when quantities are 10-20 mls; however, a volumetric addition funnel will be needed. The pressure in bottles of air sensitive chemicals must be tightly controlled. Never draw out pyrophoric liquid because it might draw air into the reagent bottle. A blanket of nitrogen or argon gas needs to be kept over the air sensitive chemicals. Use a long flexible needle that is one to two feet long to transfer liquid via the cannula method. Check the syringe for any leaks - you do not want to discover that the syringe with pyrophoric liquid has a leak and is on fire. Consider using the needle just one time so it does not clog (leaving you holding a syringe of pyrophoric liquid). When you transfer large volumes of pyrophoric material, arrange for someone to be watching you in case an accident should occur. Others in the lab should know that you will be working with pyrophorics. It may be safer to work with pyrophoric liquids at cold temperatures because flammable liquids at room temperature are more likely to be a fire hazard.



Double tipped needle transfer of liquid reagent and the syringe transfer method are demonstrated in photos and drawings at the end of this document.

3.4 Storage and Disposal

Storage

- Use and store minimal amounts of reactive chemicals. Do not store reactive chemicals with flammable materials or in a flammable liquids storage cabinet. Containers carrying reactive materials must be clearly labeled with the correct chemical name and hazard warning in English.
- Store reactive materials as recommended in the SDS or product guidance. Inert gas-filled desiccators or glove boxes are suitable storage locations for most materials. Refrigerated material should be stored in non-combustible containment, away from flammables.
- Ensure that a sufficient protective solvent, oil, kerosene, or inert gas remains in the container while the material is stored.
- NEVER return any excess chemical to the original container. Small amounts of impurities introduced into the container may cause a fire or explosion. Excess material can be used up as part of the experimental procedure or quenched using an appropriate technique.
- For storage of any excess chemical, prepare a storage vessel in the following manner:
  - Dry any new empty containers thoroughly (i.e.in an oven).
  - Insert the septum into the neck in a way that prevents atmosphere from entering the clean, dry (or reagent filled) flask.
  - Insert a needle to vent the flask and quickly inject inert gas through a second needle to maintain a blanket of dry inert gas above the reactive reagent.
  - Once the vessel is fully purged with inert gas, remove the vent needle then the gas line. To introduce the excess chemical, use the procedure described in the handling section, below.
- For long-term storage, the septum should be secured with a copper wire (figure 1A).
- For extra protection a second same-sized septa (without holes) can be placed over the first (figure 1b).
- Use parafilm around the outer septa; remove the parafilm and outer septum before accessing the reagent through the primary septum.

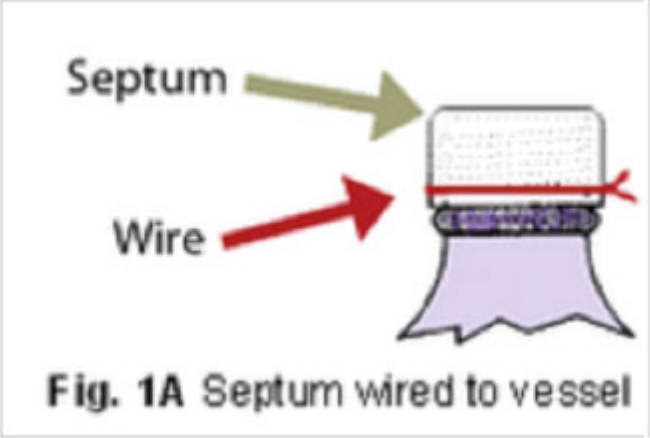


Fig. 1A Septum wired to vessel

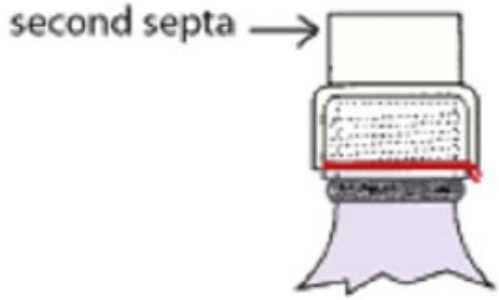


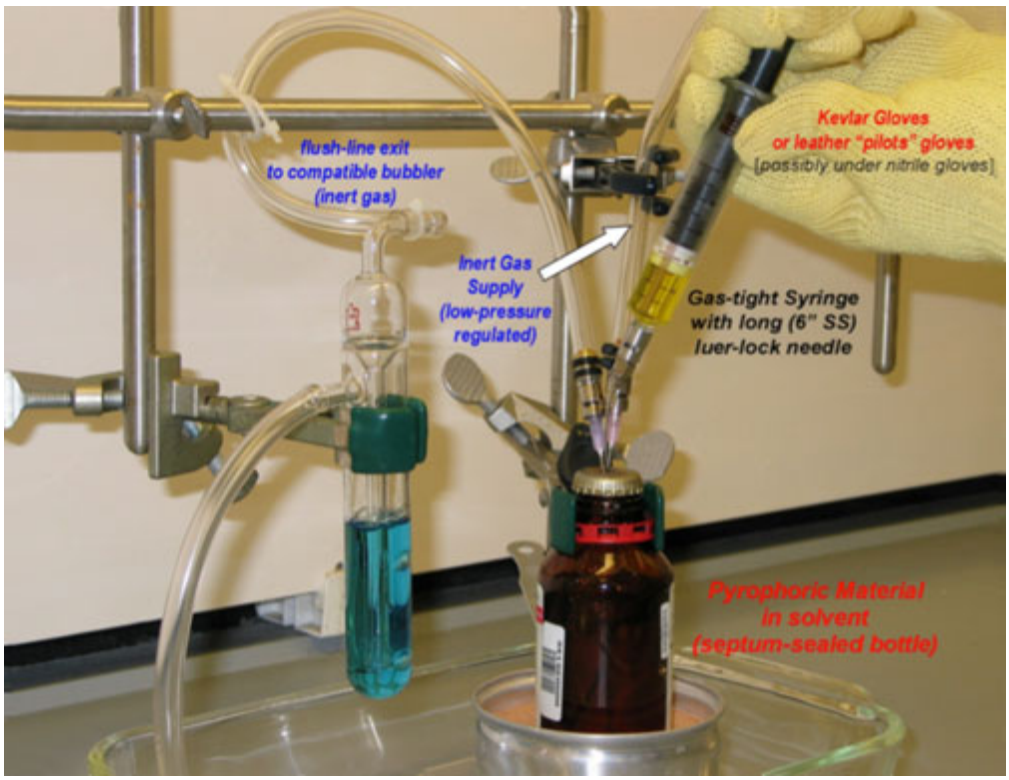
Fig. 1B For long-term storage, use a second septum

Disposal of Pyrophoric Reagents

- Any container with a residue of hazardous reactive materials should never be left open to the atmosphere.
- Any unused or unwanted air reactive materials must be destroyed by transferring the materials to an appropriate reaction flask for hydrolysis and/or neutralization with adequate cooling. The empty container should be rinsed three times with an inert dry COMPATIBLE solvent; this rinse solvent must also be neutralized or hydrolyzed. Neutralization should be done in cold bath to better control the neutralization. The rinse solvent must be added to and removed from the container under an inert atmosphere.
- After the empty container is triple-rinsed, it should be left open in back of a hood or ambient atmosphere at a safe location for about a week.
- The empty container, solvent rinses and water rinse should be disposed of 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 of as hazardous waste. Proper and complete hazardous waste labeling of containers is important.
- The contaminated waste should be placed in a metal container away from other combustibles to prevent fires. Verify the material is no longer pyrophoric before placing waste in with other combustible waste.



Syringe transfer method for small quantities of pyroforic liquids

4 References

- OSHA 3404-11R (2011) – Laboratory Safety Guidance
- KAUST Laboratory Safety Manual
- HSE-RST-Chem001M – Chemical Safety Program
- UC Berkeley EHS

5 Help

Questions about this guideline? Contact: hse@kaust.edu.sa