

Safe Use of Pyrophoric/Water Reactive Materials

Introduction

Pyrophoric and water reactive materials can ignite spontaneously on contact with air, moisture in the air, oxygen, or water. Failure to follow proper handling procedures can result in fire or explosion, leading to serious injuries, death and/or significant damage to facilities.

In December 2008, a laboratory accident at UCLA occurred while the researcher was working with *t*-butyllithium, a highly pyrophoric agent which resulted in the researcher's death.

Any handling of a pyrophoric/water reactive material is high risk and must be controlled with adequate system design, direct supervision and training. These tasks are two person tasks and workers should not work alone.

Good technical guidance can be found in **Aldrich Technical Bulletins AL-134 and AL-164** (<http://www.sigmaaldrich.com/chemistry/aldrich-chemistry/tech-bulletins.html>)

Examples of Pyrophoric/Water Reactive Materials

Grignard Reagents: RMgX (R=alkyl, X=halogen)

Metal alkyls and aryls: Alkyl lithium compounds; *tert*-butyllithium; Tributylaluminum

Metal carbonyls: Lithium carbonyl, nickel tetracarbonyl

Metal powders (finely divided): Cobalt, iron, zinc, zirconium

Metal hydrides: Sodium hydride, lithium aluminum hydride

Nonmetal hydrides: Diethylarsine, diethylphosphine

Non-metal alkyls: R_3B , R_3P , R_3As ; tetramethylsilane, tributylphosphine

White and red phosphorus

Group I (Alkali) metals: Lithium, potassium, sodium, sodium-potassium alloy (NaK), rubidium, cesium, francium

Gases: Silane, dichlorosilane, diborane, phosphine, arsine

Hazards

Because these reagents ignite 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. Some are toxic and many come dissolved or immersed in a flammable solvent. Other common hazards include corrosivity, teratogenicity, water reactivity, or peroxide formation, and may damage to the liver, kidneys, and central nervous system.

Controlling the Hazards

BEFORE working with pyrophoric or water reactive reagents, read the relevant Material Safety Data Sheets (MSDS), technical bulletins, and guidance documents to understand how to mitigate the hazards. The MSDS 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. ALWAYS wear the appropriate 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 risk if a fire should occur. Keep combustible materials, including paper towels and Kimwipes, away from reactive reagents.

Keep the amount of pyrophoric or water reactive material present in your lab to the smallest amount practical. Use and handle the smallest quantity practical. It is better to do multiple transfers of small volumes than attempt to handle larger quantities (greater than about 20 mL).

Alternatively, an appropriately engineered system, capable of safely handling the larger quantity must be designed, tested and properly used.

Personal Protective Equipment (PPE)

Eye Protection

- Chemical Splash goggles or safety glasses must be worn whenever handling pyrophoric chemicals. Prescription eye glasses, safety glasses, and splash goggles will NOT provide adequate protection. A face shield, worn over safety eyewear, is required any time there is a risk of explosion, splash hazard or a highly exothermic reaction.

Skin Protection

- Gloves should be worn when handling pyrophoric chemicals. Nitrile gloves should be adequate for handling most of these in general laboratory settings. Sigma-Aldrich recommends the use of nitrile gloves underneath neoprene gloves. An MSDS should be reviewed if handling may involve extended or high exposure to lab personnel to ensure adequate skin protection is provided.
- Avoid wearing synthetic clothing while working with pyrophorics. **A lab coat or apron (not made from easily ignited material like nylon or polyester) must be worn.** Special fire-resistant lab coats made from Nomex are more expensive, but only recommended for labs using these reagents routinely.
- No open toe shoes are allowed.

Safety Equipment

Researchers working with reactive materials must have the proper equipment and the emergency phone number (9-1-1) readily available for any emergencies, prior to starting research activities. Acceptable extinguishing media include soda ash (lime) or *dry* sand to respond to fires. **DO NOT** use water to attempt to extinguish a pyrophoric/reactive material fire as it can actually enhance the combustion of some of these materials, e.g. metal compounds. A small beaker of 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. Review the MSDS for the proper fire extinguisher to use with the given material.

Eyewash/ Safety Shower

- A combination eyewash/safety shower should be inside the laboratory.
- If a combination eyewash/safety shower is not available within the lab, an eyewash must be available for immediate emergency use within the lab. Bottle type eyewash stations are not acceptable. A safety shower must be available in the hallway or similar, within 10 seconds travel distance and accessible through only one door.
- Ensure that lab personnel know the locations of eyewashes and safety showers and the most direct route to access them.

Fume Hood

- Many reactive chemicals release noxious or flammable gases upon decomposition and should be handled in a laboratory 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.

Glove (dry) box

- Inert atmosphere glove boxes are an excellent device 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 introduction of reactive compounds into the box. 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).

- If the potential exists for explosion or a high thermal reaction, additional shielding should be utilized. This may involve the use of shielding in a glove box or in the case of a fume hood with the sash in the lowest possible position. Portable shields may also be used for additional protection.

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, in English, and hazard warning.
- Store reactive materials as recommended in the MSDS. An inert gas-filled desiccator or glove box is a suitable storage location for most materials.
- If pyrophoric or water reactive reagents are received in a specially designed shipping, storage or dispensing container (such as the Aldrich Sure/Seal packaging system) ensure that the integrity of that container is maintained.
- Ensure that sufficient protective solvent, oil, kerosene, or inert gas remains in the container while the material is stored.
- NEVER return excess chemical to the original container. Small amounts of impurities introduced into the container may cause a fire or explosion.

Disposal of Pyrophoric Reagents

- Any container with a residue of reactive materials should never be left open to the atmosphere.
- All materials that contain or are contaminated with pyrophoric chemicals should be disposed of as hazardous waste.
- Proper and complete hazardous waste labeling of containers is vital.
- A container with residual material must NEVER be opened to the atmosphere.
- If the pyrophoric chemical was originally stored in solvent and is dried, hydrate the chemical with an appropriate solvent before pick-up. The best solvent to use is the same solvent used for the solution of the original reagent.

Important Steps to Follow

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 must 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. See Attachment 1. Another good reference is “Manipulation of Air-sensitive Compounds” by Shriver and Drezdson.

Handling Pyrophoric Liquids

- Users should read and understand the Aldrich Technical Information Bulletin No. AL-134. See Attachment 1. The PI should also have in place laboratory-specific handling, storage, and disposal standard operating procedures. The standard operating procedures should be included in the lab SOP Manual.
- By using proper syringe techniques, these reagents can be handled safely in the laboratory. The Aldrich Sure/Seal™ Packaging System provides a convenient method for storing and dispensing air-sensitive reagents. Schlenk glassware is another suitable option.
- The reagent can be dispensed using a syringe or double-tipped needle (canula) (16, 18 or 20 gauge) inserted through the hole in the metal cap, as shown in fig. 2 below. It is recommended that the plastic cap be replaced after each use and in particular for long-term storage.

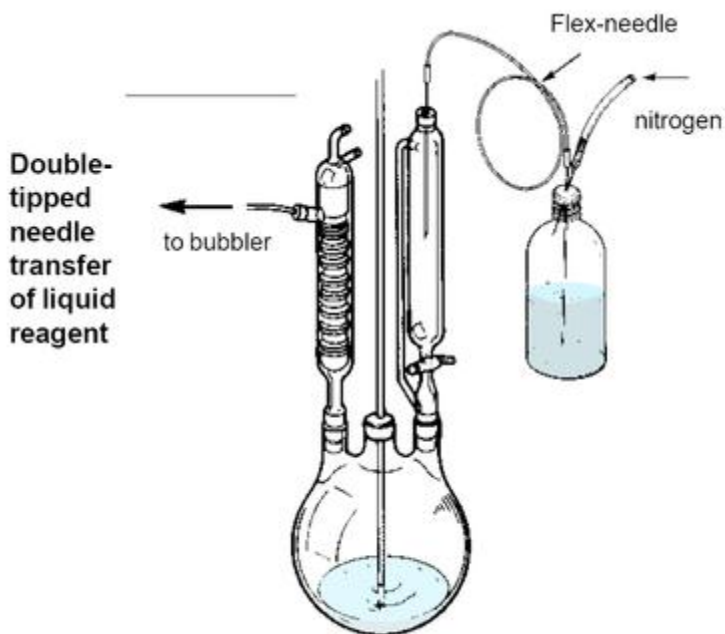


Fig. 2 Double-tipped needle transfer of liquid reagent

- 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 above.

Emergency Procedures

Spill

- DO NOT use water to attempt to extinguish a reactive material fire as it can actually enhance the combustion of some reactive materials, e.g. metal compounds.
- Do not use combustible materials (paper towels) to clean up a spill, as these may increase the risk of igniting the reactive compound. Soda ash (powdered lime) or dry sand should be used to completely smother and cover any small spill that occurs.
- A container of soda ash (powdered lime) or dry sand should be kept within arm's length when working with a reactive material.
- If anyone is exposed, or on fire, wash with copious amounts of water, except if metal compounds are involved, which can react violently with water. In the case of a metal fire, smothering the fire is a better course of action.
- The recommended fire extinguisher is a standard dry powder (ABC) type. Class D extinguishers are recommended for combustible solid metal fires (e.g. sodium, LAH), but not for organolithium reagents. Contact the Fire Department and review the MSDS for the appropriate fire extinguisher.

- Call 9-1-1 for emergency assistance and for assistance with all fires, even if extinguished.
- Pyrophoric gas releases and associated fires, should be extinguished by remotely stopping the gas flow. NEVER ATTEMPT TO PUT OUT A GAS FIRE IF THE GAS IS FLOWING.

Attachment 1

Excerpt from the Sigma-Aldrich Technical Bulletins AL-134 and AL-164 at:

<http://www.sigmaaldrich.com/chemistry/aldrich-chemistry/tech-bulletins/tech-bulletin-numbers.html>

The Aldrichⁱ Sure/Seal™ Packaging System

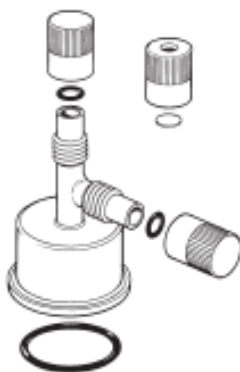


Fig. 1B Sure/Seal septum-inlet transfer

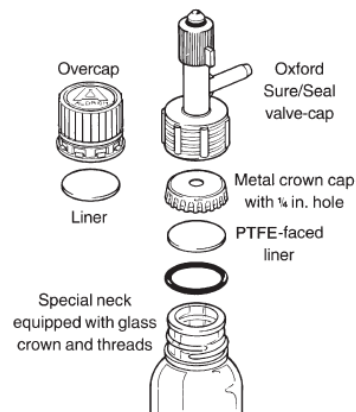


Fig. 1A Sure/Seal components

adapter

The Sure/Seal packaging system (**Fig. 1A**) provides a convenient method for storing and dispensing air-sensitive reagents. The reagent can be dispensed using a syringe or double-tipped needle (16, 18 or 20 gauge) inserted through the hole in the metal cap. When inserting a needle through a septum, a layer of silicone or hydrocarbon grease on the septum will help. Upon withdrawal of the needle, the small hole that remains in the PTFE liner will not cause the reagent to deteriorate under normal circumstances. However, it is recommended that the plastic cap be replaced after each use and in particular for long-term storage.

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.

The Sure/Seal septum-inlet transfer adapter (**Fig. 1B**) can be used when repeated dispensing is necessary. The adapter protects the contents of the bottles from air and moisture.

Transferring Pyrophoric Reagents with Syringe

- In a fume hood or glove box, clamp the reagent bottle to prevent it from moving
- Clamp/secure the receiving vessel too.
- After flushing the syringe with inert gas, depress the plunger and insert the syringe into the Sure/Seal bottle with the tip of the needle below the level of the liquid
- Secure the syringe so if the plunger blows out of the body it, and the contents will not impact anyone (aim it toward the back of the containment)
- Insert a needle from an inert gas source carefully keeping the tip of the needle above the level of the liquid
- Gently open the inert gas flow control valve to slowly add nitrogen gas into the Sure/Seal bottle.
- This will allow the liquid to slowly fill the syringe (up to 100mL) as shown in **Fig. 2A**. Pulling the plunger causes gas bubbles.

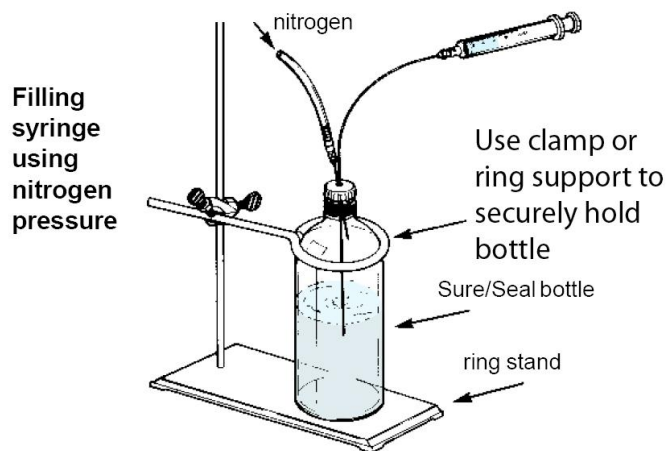


Fig. 2A Filling syringe using nitrogen pressure

- Let nitrogen pressure push the plunger to reduce bubbles. Excess reagent and entrained bubbles are then forced back into the reagent bottle as shown in **Fig. 2B**.
- The desired volume of reagent in the syringe is quickly transferred to the reaction apparatus by puncturing a rubber septum as illustrated in **Fig. 2C**.

Removing gas bubbles and returning excess reagent to the Sure/Seal bottle

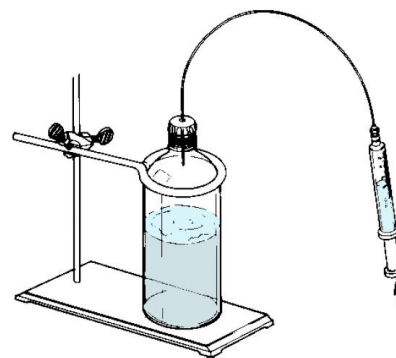


Fig. 2B Removing gas bubbles and returning excess reagent to the Sure/Seal bottle

Syringe transfer of reagent to reaction vessel

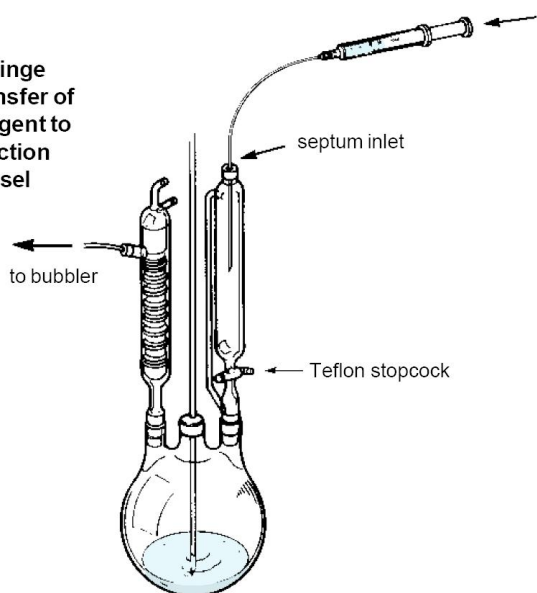


Fig. 2C Syringe transfer of reagent to reaction vessel

Double-tipped needle transfer of liquid reagent

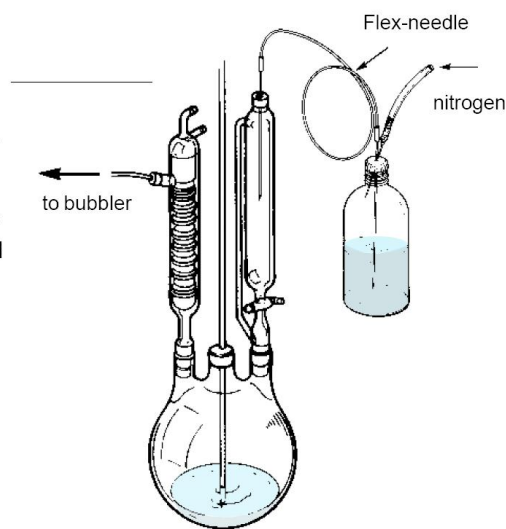


Fig. 3A Double-tipped needle transfer of liquid reagent

Transferring Pyrophoric Reagents with a Double-Tipped Needle (Cannula)

- The double-tipped needle technique is recommended when transferring 50 mL or more.
- Pressurize the Sure/Seal bottle with nitrogen and then insert the double-tipped needle through the septum into the headspace above the reagent. Nitrogen will pass through the needle. Insert the other end through the septum at the calibrated addition funnel on the reaction apparatus. Push the needle into the liquid in the Sure/Seal reagent bottle and transfer the desired volume. Then withdraw the needle to above the liquid level. Allow nitrogen to flush the needle. Remove the needle first from the reaction apparatus and then from the reagent bottle. **(Fig. 3A)**
- For an exact measured transfer, convey from the Sure/Seal bottle to a dry nitrogen flushed graduated cylinder fitted with a double-inlet adapter **(Fig. 3B)**. Transfer the desired quantity and then remove the needle from the Sure/Seal bottle and insert it through the septum on the reaction apparatus. Apply nitrogen pressure as before and the measured quantity of reagent is added to the reaction flask.
- To control flow rate, fit a Luer lock syringe valve between two long needles as shown in **(Fig. 3C)**.

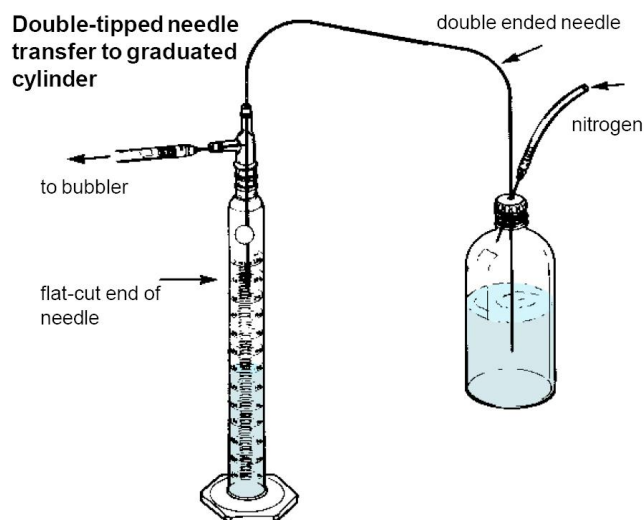


Fig. 3B Double-tipped needle transfer to graduated cylinder

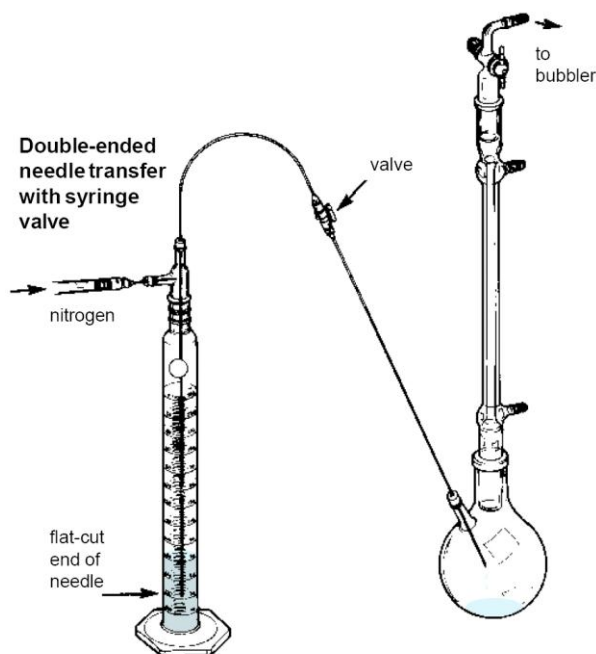


Fig. 3C Double-ended needle transfer with syringe valve

Sources and Acknowledgements:

Created from a variety of sources including: Brandeis University, Standard Operating Procedure for Pyrophoric Chemicals; University of Nebraska, Lincoln, Pyrophoric Chemicals Standard Operating Procedure; University of Pittsburgh Safety Manual, Flammable and Pyrophoric Gas; Rochester University, SOP for Pyrophoric Chemicals. Images from Sigma-Aldrich Technical Bulletins [AL-134](#) and [AL-164](#). UC Davis Procedures Safe Use of Pyrophoric reagents.

ⁱ Images and advice from Sigma-Aldrich Technical Bulletins

⁴ Destruction of Hazardous Chemicals in the Laboratory ,George Lunn, Eric B. Sansone ,Wiley-Interscience; 2nd edition (March 1994) , ISBN: 047157399X

Additional References:

Leonard J., B. Lygo, and G. Procter, Advanced practical organic chemistry. London : Blackie ; New York : Chapman and Hall, 1995, pages 76-98.

Prudent Practices in the Laboratory: Handling and Disposal of Chemicals , National Research Council
Publisher: National Academies Press; 1 edition (January 10, 2000), ISBN: 0309052297

We wish to acknowledge the following sources: Brandeis University, Standard Operating Procedure for Pyrophoric Chemicals; University of Nebraska, Lincoln, Pyrophoric Chemicals Standard Operating Procedure; University of Pittsburgh Safety Manual, Flammable and Pyrophoric Gas; Rochester University, SOP for Pyrophoric Chemicals.