

Procedures for Safe Use of Pyrophoric Liquid Reagents

Researchers should not use pyrophoric reagents until they have read and fully understood these safe operating procedures. However, reading these procedures does not substitute for hands-on training. New users of pyrophoric reagents must work under the close supervision of an experienced user.

I. Scope

A variety of liquid reagents are pyrophoric (spontaneously ignite in air) including (but not necessarily limited to):

- Alkylolithium reagents (Typically in hydrocarbon solvents) (*Tert*-butyllithium is VERY pyrophoric)
- Alkenyllithium and Aryllithium reagents (Typically in hydrocarbon solvents)
- Alkynyllithium reagents (Typically in hydrocarbon solvents)
- Grignard Reagents (RMgX) (Typically in hydrocarbon solvents)
- Alkylaluminum reagents (Neat or in hydrocarbon solvents) (Neat reagents are VERY pyrophoric)
- Alkylzinc reagents (Neat reagents are pyrophoric)
- Boranes (Neat reagents are pyrophoric)

II. Hazards

In general these materials are pyrophoric; they ignite spontaneously when exposed to air. They also tend to be associated with flammable solvents. Other common hazards include corrosivity, water reactivity, peroxide formation, toxicity, and damage to the liver, kidneys, and central nervous system.

III. Controlling the Hazards

BEFORE working with pyrophoric reagents, read the relevant Material Safety Data Sheets (MSDS) and understand the hazards. The MSDS must be reviewed before using an unfamiliar chemical and periodically as a reminder.

Set up your work in a laboratory fume hood or glove box and ALWAYS wear the appropriate PPE

Personal Protective Equipment (PPE)

Eye Protection

- Chemical Splash goggles or safety glasses that meet the ANSI Z.87.1 1989 standard must be worn whenever handling pyrophoric chemicals. Ordinary prescription glasses will NOT provide adequate protection unless they also meet this standard. When there is the potential for splashes, goggles must be worn, and when appropriate, a face shield added.
- A face shield is required any time there is a risk of explosion, large splash hazard or a highly exothermic reaction. All manipulations of pyrophoric chemicals which pose this risk should occur in a fume hood with the sash in the lowest feasible position. Portable shields, which provide protection to all laboratory occupants, are acceptable.

Skin Protection

- Gloves must be worn when handling pyrophoric chemicals. Nitrile gloves should be adequate for handling most of these in general laboratory settings but they are combustible. Use adequate protection to prevent skin exposures. Heavy gloves are required for work with large quantities.
- *A fire resistant lab coat must be worn.*
- A chemical-resistant apron worn over the lab coat is required for working with large quantities.
- No open toe shoes are allowed.

IV. Designated Work Area

Eyewash

- Suitable facilities for quick drenching or flushing of the eyes should be within 10 seconds travel time for immediate emergency use. Bottle type eyewash stations are not acceptable.

Safety Shower

- A safety or drench shower should be available within 10 seconds travel time where pyrophoric chemicals are used.

Fume Hood

- Many pyrophoric chemicals release noxious or flammable gases 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.

Fire Extinguisher

- A Class C dry chemical fire extinguisher must be available within 10 seconds travel time from where pyrophoric chemicals are used.
- Know the location of the nearest Class D fire extinguisher.
- A container of powdered lime (calcium oxide, CaO) should be kept within arm's length when working with a pyrophoric material.

Glove (dry) box

- Glove boxes are an excellent device to control pyrophoric chemicals when inert or dry atmospheres are required.

V. Protocols

Handling pyrophoric Reagents

By using proper needle and syringe techniques, these reagents can be handled safely in the laboratory.

The Aldrich¹ Sure/Seal™ Packaging System

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.

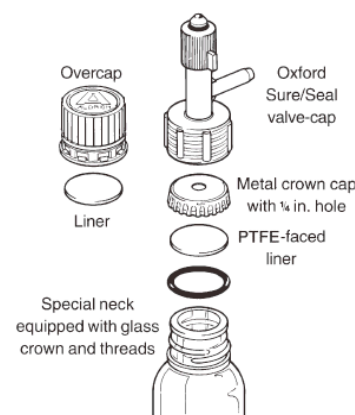


Fig. 1A Sure/Seal components

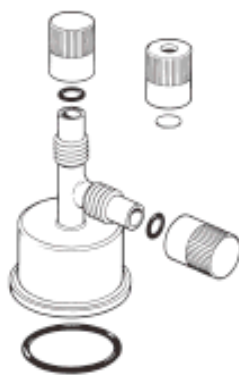


Fig. 1B Sure/Seal septum-inlet transfer adapter

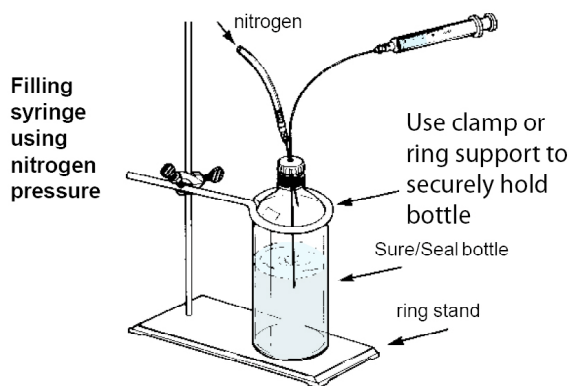


Fig. 2A Filling syringe

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

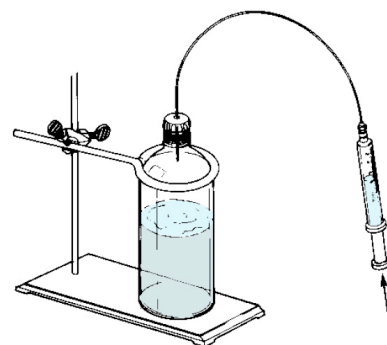


Fig. 2B Removing gas bubbles and returning excess reagent to the Sure/Seal bottle

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 bottle keeping the needle tip above the liquid level.
- NOTE: The goal of this technique is to equalize the pressure in the reagent bottle. A different technique is to use inert gas pressure to force reagent into the syringe, but that has the danger of blowing the plunger out of the syringe body and spilling out pyrophoric reagent.
- Flush dry syringe with inert gas, 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 (Fig. 2A). Pulling too hard or too fast can cause air bubbles to enter between the plunger and syringe body.
- NOTES: Simple glass syringes are more prone to causing gas bubbles. Disposable plastic syringes have a good seal on the plunger and work well. Glass syringes with Teflon-tipped plungers (gas-tight) syringes are best. For safest work, do not fill syringe more than 60% full, up to a maximum of 10 mL of liquid. The double-tipped needle technique is safer when transferring 10 mL or more.
- Excess reagent and entrained bubbles are then forced back into the reagent bottle (Fig. 2B).
- 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 (Fig. 2B) 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 as illustrated in Fig. 2C.

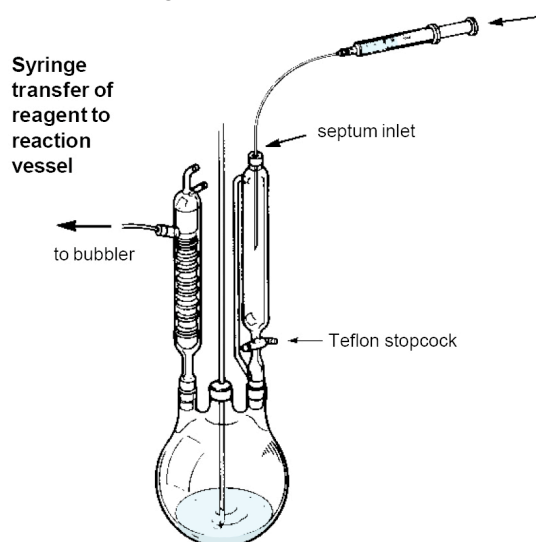


Fig. 2C Syringe transfer of reagent to reaction vessel

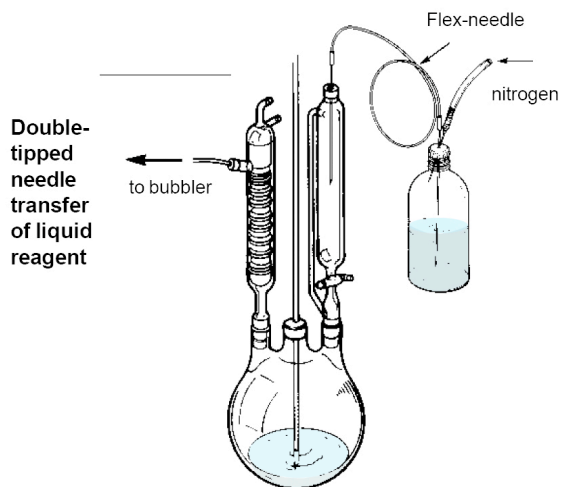


Fig. 3A Double-tipped needle transfer of liquid reagent

Transferring Pyrophoric Reagents with a Double-Tipped Needle

- The double-tipped needle technique is recommended when transferring 10 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 which must be equipped with a gas line to a bubbler. 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**)
- Alternatively, 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**).

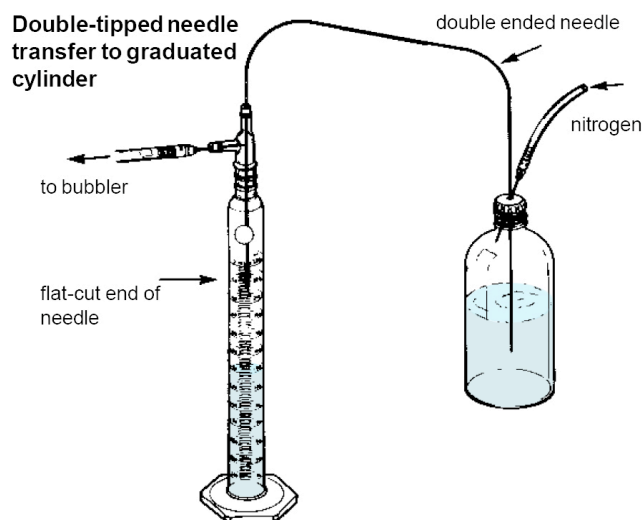


Fig. 3B Double-tipped needle transfer to graduated cylinder

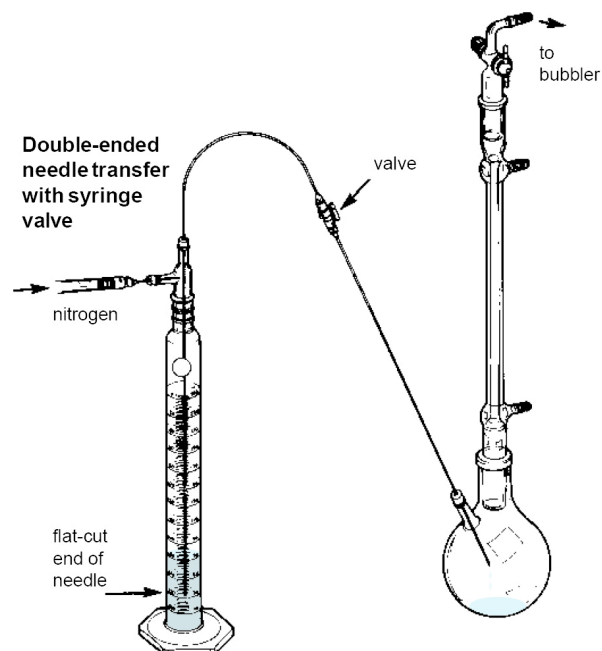


Fig. 3C Double-ended needle transfer with syringe valve

Cleaning Pyrophoric Reagents from Needles and Syringes

- Needles and syringes used with pyrophoric reagents must be cleaned immediately to avoid clogging the needles and seizing the syringes.
- Draw hexane into the syringe containing small amounts of pyrophoric reagent and then discharge the diluted solution into isopropanol.
- Similarly, flush double-tipped needles with hexane and then quench hexane wash in isopropanol.

Storage

- Store pyrophoric chemicals under an inert atmosphere or under kerosene as appropriate.
- Avoid areas with heat/flames, oxidizers, and water sources.
- Containers carrying pyrophoric materials must be clearly labeled with the correct chemical name and hazard warning.

Disposal of Pyrophoric Reagents

- Small amounts of unused or unwanted pyrophoric materials must be destroyed by careful quenching of the residue. Transfer the materials to an appropriate reaction flask for hydrolysis and/or neutralization. Dilute significantly with an unreactive solvent such as heptane or toluene and place the flask in an ice water cooling bath. Slowly add isopropanol to quench pyrophoric materials. Upon completion, add methanol as a more reactive quenching agent to ensure completion. Finally, add water dropwise to make sure there are no pockets of reactive materials. Dispose of as hazardous waste.
- Alternatively, reactive substances can be quenched by slowly adding the dilute solution to dry ice, then adding a mildly reactive quenching agent such as methanol.
- AVOID low boiling diluents such as ether and pentane that tend to condense water upon evaporation.
- Do not leave containers with residues of pyrophoric materials open to the atmosphere due to uncontrolled ignition.

Disposal of Pyrophoric Solid Reagents by Submitting to EHS as Hazardous Waste

- Larger quantities of pyrophoric chemicals can be disposed of as hazardous waste.
- Carefully package and label the wastes.
- **Specifically Alert** EH&S personnel at the collection location to the hazards of any wastes containing pyrophoric chemicals.

VI. Emergency Procedures

Spill - Small

- Exert extreme caution due to potential spontaneous combustion.
- Exert extreme caution due to potential ignition of flammable solvents or other materials.
- If anyone is exposed, or on fire, wash with copious amounts of water, ideally in the lab shower.
- Call for a coworker to provide backup.
- Place a fire extinguisher nearby.
- Carefully remove nearby flammable materials.
- Powdered lime (calcium oxide, CaO) or dry sand should be used to completely smother and cover any spill that occurs.
- Carefully quench by slow addition of isopropanol.
- After complete quench, double bag spill residues for hazardous waste pickup.
- Call 911 for emergency assistance if necessary.

Spill - Large

- Exert extreme caution due to potential spontaneous combustion.
- Exert extreme caution due to potential ignition of flammable solvents or other materials.
- If anyone is exposed, or on fire, wash with copious amounts of water, ideally in the lab shower.
- Call 911 for emergency assistance.
- Evacuate the spill area.
- Post someone or mark-off the hazardous area with tape and warning signs to keep other people from entering.
- Provide emergency personnel with technical advice on the chemicals involved.

Images and advice from Sigma-Aldrich Technical Bulletins AL-134 and AL-164 at:

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