

Techniques for Handling Air- and Moisture-Sensitive Compounds

- *Introduction*
- *The Glove Box*
- *Schlenk Techniques*
- *Drying and Degassing Solvents*

1

What are Air-Sensitive Compounds?

Materials which oxidize, decompose or even explode under the influence of oxygen or moisture.

- Pyrophoric Compounds
 - Metal alkyls and aryls e.g. RMgX , RLi , RNa , R_3Al , R_2Zn
 - Metal carbonyls e.g. $\text{Ni}(\text{CO})_4$, $\text{Fe}(\text{CO})_5$, $\text{Co}_2(\text{CO})_8$
 - Alkali metals e.g. Na , K , Cs
 - Metal powders e.g. Al , Co , Fe , Mg , Pd , Pt , Zn
 - Metal hydrides e.g. NaH , KH , LiAlH_4
 - Hydrides e.g. B_2H_6 , PH_3 , AsH_3
 - Boranes, phosphines, arsenes, etc. e.g. Et_3B , R_3P , R_3As
- Chemicals which react violently with water
 - Metal hydrides, metal amides (NaNH_2), metal alkyls and aryls, metals, metal powders, hydrides, many main group halides (BCl_3 , BF_3 , AlCl_3 , PCl_3 , SiCl_4), inorganic acid halides (POCl_3 , SOCl_2), low molecular weight organic acid halides and anhydrides.

Glove boxes and Schlenk techniques do NOT protect from explosive or shock sensitive materials or mixtures!!! Also, they only provide limited protection from toxic compounds.

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The Glove Box

- The best way to keep things away from atmospheric oxygen and water is to work in a fully enclosed “bench top,” containing an “inert atmosphere,” which one could reach into with gloves. Such a device is called a “glove box” or a “dry box”. There are also cheap “glove bags”, bags you can fill with inert gas and reach into with attached gloves.

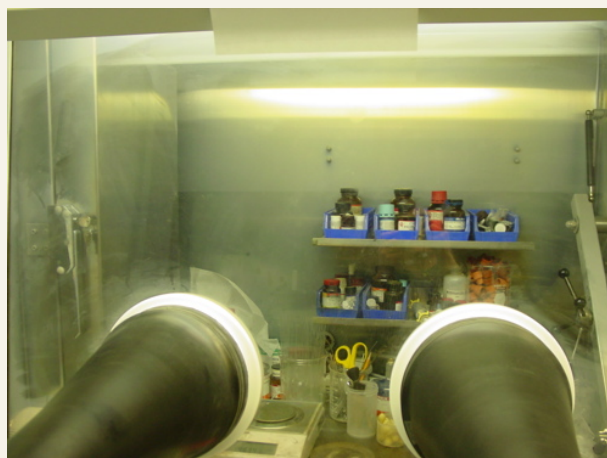


3

The Glove Box

A glove box has four important components:

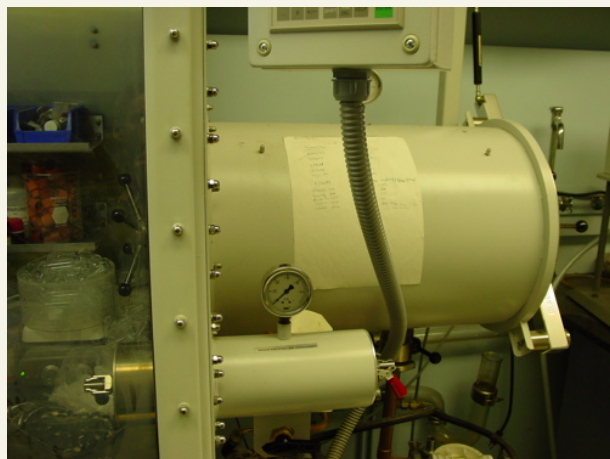
1. The actual “box” is a large aluminum chamber with a plastic front window and two impressive looking gloves. This is the working area. Organic solvents will spoil the plastic, and fancy fingerware, opulent wedding trophies, or pointy fingernails will puncture the rubber gloves and deflate the system.



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The Glove Box

- 2) There is an antechamber (like a submarine or spaceship airlock) which is how things get in and out without letting in air.

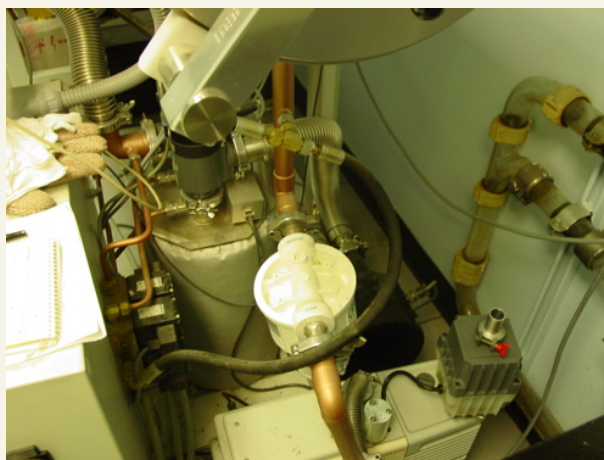


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The Glove Box

- 3) The gas in the box is constantly circulated over a scrubber (often called the "catalyst") which removes any air or water that has made its way into the enclosure. Since the catalyst is damaged by many kinds of reactive chemicals (chlorinated solvents, sulfur compounds, etc.), we must be careful what we allow to evaporate into the box atmosphere.

A fan inside the box circulates the box atmosphere through the canister.



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The Glove Box

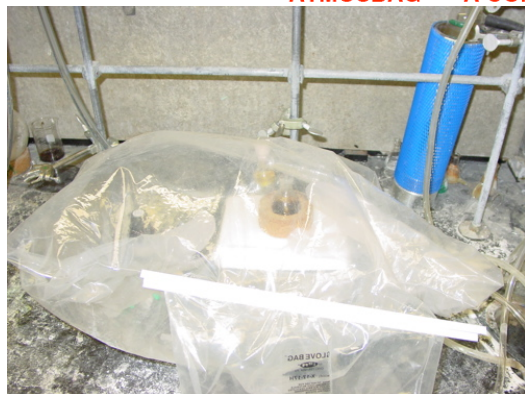
4) The glove box must be able to regulate pressure inside. The device that regulates the pressure is set to tolerate only a few millibar of positive and negative pressure and automatically pumps nitrogen out if the pressure gets too high or draws fresh nitrogen in from a tank/dewar if the pressure gets too low. One can also regulate pressure manually with a foot pedal.



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The Glove Bag

ATMOSBAG — A CONTROLLED - ATMOSPHERE CHAMBER



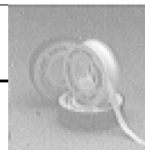
The Aldrich AtmosBag is a 0.003-in. gauge PE bag that can be sealed, purged, and inflated with an appropriate inert gas, creating a portable, convenient, and inexpensive two handed “glove box” for handling air- and moisture-sensitive as well as toxic materials. Other applications include dust-free operations, controlled-atmosphere habitat, and, for the ethylene-oxide-treated AtmosBag, immunological and microbiological studies. Small AtmosBags have one inlet per side. Includes instructions.

CAUTION: When handling toxic materials use only in a hood or other controlled system to prevent and protect against exposure in case of leakage. All products made of PE may tear, break, or puncture. To assure that air-sensitive materials do not become exposed to air, follow instructions on package; also test and monitor AtmosBag for leaks before and during use.

Size	Uninflated dimensions (in.)			Inflated volume (in.3)	Ethylene oxide treated	
	Opening	Width	Length		Cat. No.	Cat. No.
S	12	27	30	3,000 (50L)	Z11,283-6	Z11,837-0
M	24	39	48	17,000 (280L)	Z11,282-8	Z11,836-2
L	36	51	58	32,000 (520L)	Z10,608-9	Z11,835-4

Teflon sealing tape
 In 520-in. roll.

Width (in.)	Cat. No.
1/4	Z14,881-4
1/2	Z10,438-8
1	Z22,188-0



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The Dry Box



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Safe Handling of Organolithium Reagents



- Clear your bench and all working areas prior to use. Do not work alone.
- There are two options for the handling of organolithium and other highly pyrophoric reagents.
 - syringe and needle: preferred for smaller amounts of reagent.
 - cannula: safer and more practical for > 15 mL.
- http://www.sigmaldrich.com/etc/medialib/docs/Aldrich/Bulletin/altechbullal134.Par.0001.File.tmp/al_techbull_al134.pdf

University of Pittsburgh Safety Manual	EH&S Guideline Number: 04-015	
Subject: GUIDELINES FOR SAFE USE OF CHEMICAL SYRINGES	Effective Date 3/1/08	Page 1 of 1

GUIDELINES FOR SAFE USE OF CHEMICAL SYRINGES

Syringes are used in research labs for multiple tasks including injection of gases or liquids into chromatographs, chemical apparatus or animals. Syringes can range from precision micro-syringes to inexpensive disposable units. Needle-stick injuries remain a significant hazard during syringe use, but is not the subject of this guideline. See our "Needle Stick Prevention Guidelines" at www.ehs.pitt.edu. This guideline addresses proper syringe use and chemical handling to prevent eye and face injury due to syringe spray-back.

Syringe spray-back accidents typically occur when the syringe or injection needle become plugged. If the syringe becomes plugged, do not push the plunger harder. High pressures inside the syringe can cause the plunger seal to fail or the barrel to crack spraying out liquid. The following steps are recommended for safe syringe use.

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Schlenk Techniques

Wilhelm Schlenk: The Man Behind the Flask**

Thomas T. Tidwell*

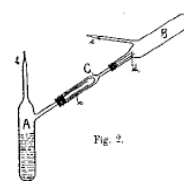
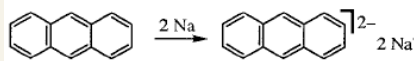


Figure 2. Left: Wilhelm Schlenk (about 1905); right: Schlenk family (1915): sister Augusta, Hermann, Emile, Wilhelm, Georg, Oskar, (courtesy of Edward Schlenk).

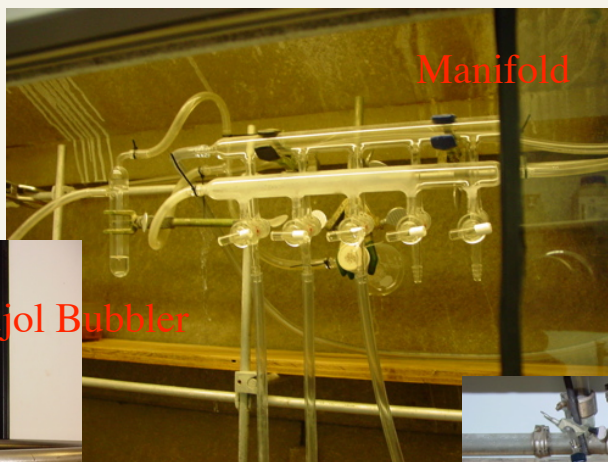
Tidwell, T. T. *Angew. Chem. Int. Ed.* 2001, 40, 331-337.

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Schlenk Techniques

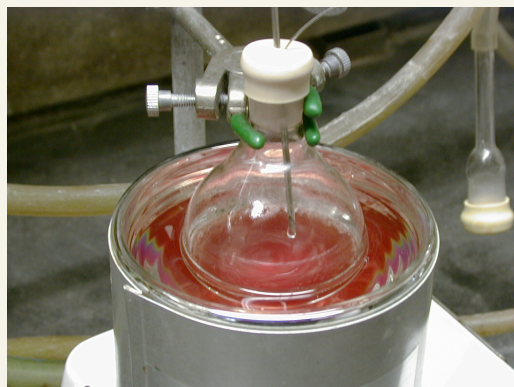
The centerpiece of an efficient defense against atmospheric intrusion outside the glove box is the double manifold, or the Schlenk line.

See http://www.sigmaaldrich.com/etc/medialib/docs/Aldrich/Bulletin/altechbullal134.Par.0001.File.tmp/al_techbull_al134.pdf for a detailed procedure on proper Schlenk techniques.



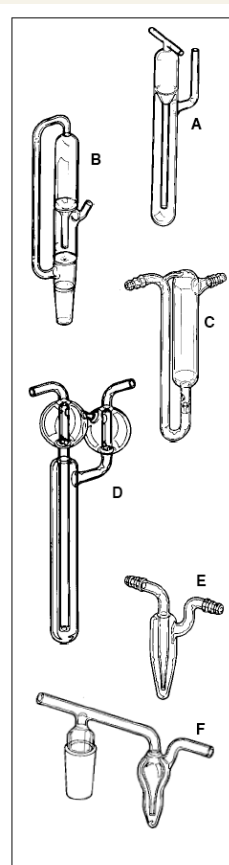
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Schlenk Techniques



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Bubblers



Standard

Mineral oil or mercury, 5-7ml. For monitoring gas evolution or rate of flow, or closing off a reaction vessel from the atmosphere. Model (b) has a $\text{F}24/40$ joint.

A Z10,121-4
 B Z10,432-9

Check-valve bubblers

Permits gas flow under positive pressure. Check-valve ball seats on ground surface under negative pressure preventing oil from being drawn into the purged system. Single inlet tube, top outlet

C Z22,501-0

T inlet tube, side outlet

Z22,502-9

Safety bubbler

The built-in flash arrester bulbs prevents the backflow of mercury and mineral oil to pumps and prevents reactions due to overflow or violent bubbling. 15ml maximum fill mark prevents over-filling.

D Z22,372-7

Mini gas bubbler

For bubble counting. Maximum volume is 4ml.

E Z22,371-9

In-line oil bubblers

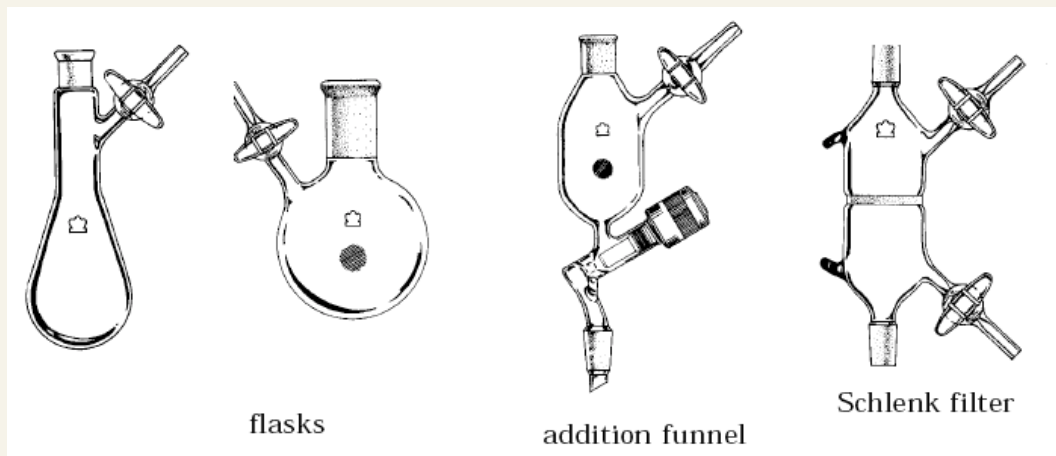
For precise N_2 pressure control during inert atmosphere reactions. Connect reaction vessel to in-line F joint or use with a ballast bulb to keep pressure constant.

F 14/20 joint F Z22,322-0
 F 19/38 joint Z22,334-4
 F 24/40 joint Z22,335-2

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Schlenk Techniques

The Schlenk flask is an ordinary round-bottom flask with a sidearm with a stopcock (greased!). You can connect this sidearm to the Schlenk line with thick rubber tubing and use it to admit nitrogen to the flask or to evacuate it. The tubing needs to be thick so that it will not collapse under vacuum. Put something in the neck of the flask, such as a septa or glass stopper (with teflon sleeves or PTFE sealing rings) or another piece of apparatus such as a Schlenk addition funnel or a Schlenk filter.



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Schlenk Techniques: Syringes

EH&S Guideline Number: 04-015

Syringes for transferring reactive chemical solutions should be gastight, greaseless, glass and have inert luer locks for use with stainless needles of appropriate ID:

Nonetheless, leakage from the piston can be a problem, particularly with volatile solvents. Gastight syringes with a PTFE sealing ring on the glass piston address this problem, albeit at the cost of adding some additional resistance while moving the piston:



Ganzglasspritze 2.0
- gasdicht mit PTFE-Dichtring
- mit metallfreiem Luer-Lock

All-glass syringe 2.0
- gastight with PTFE-ring
- with metal-free luer-lock



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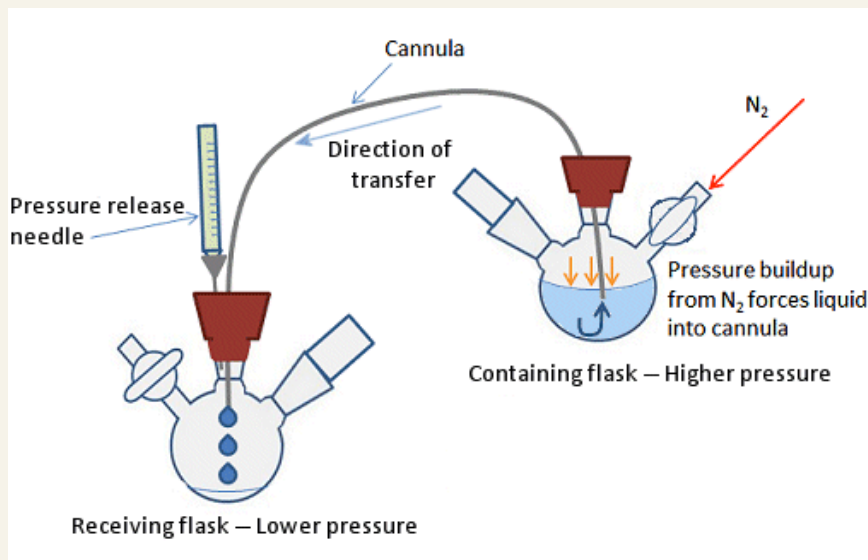
Schlenk Techniques

Convenient ways to transfer solutions into and from Schlenk flasks are via septa and syringes or cannula.

A cannula is a hollow steel needle with two sharp ends. It can serve for transferring liquids when set up as shown.

If the pressure in the flask at the right is greater than that in the other flask, the liquid will be pushed from the right to the left flask.

This pressure difference can be achieved by placing one flask under nitrogen and partially evacuating the other.



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Schlenk Techniques

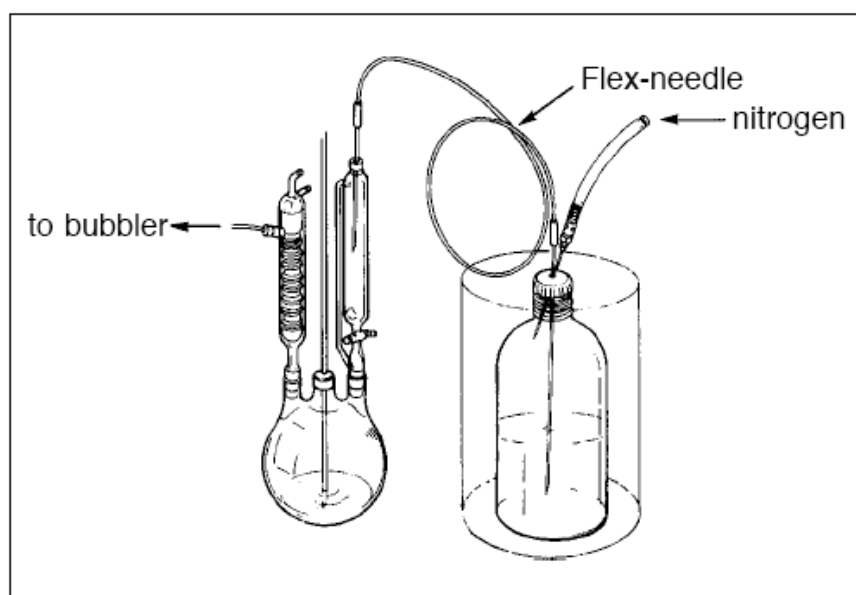


Fig. 2 Double-tipped needle transfer of pyrophoric liquid.

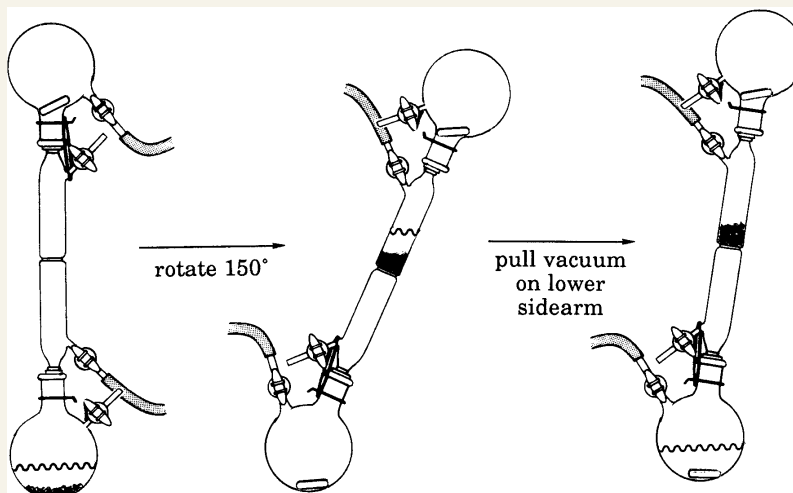
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Schlenk Techniques

To address the difficult task of no-air filtrations, the Schlenk filter (illustrated below) can be used. Its effective use requires some practice and "good hands". The filter is placed on top of the flask with the material to be filtered, and on top of it is placed a flask in which to catch the filtrate. The whole assemblage is then inverted, and you try to get as much of the solid as possible to run down on to the fritted glass disk. You can help the solid down with the stir bar,

which you can move around with a hand-held magnet on the outside of the flask.

Applying a touch of vacuum to the underside of the frit while the top is under nitrogen will move the filtrate through just like in an ordinary suction filtration.

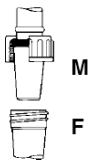


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Schlenk Techniques

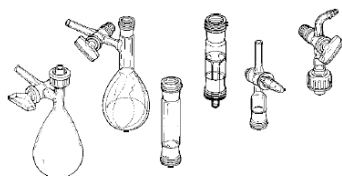
Aldrich Schlenk-type Glassware

- Request Technical Bulletin AL-166

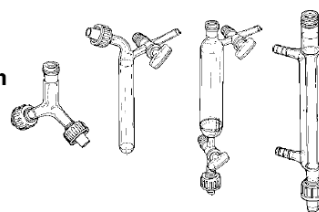


Aldrich Schlenk-type glassware features threaded ground glass joints. They require no grease, thus eliminating it as a potential contaminant, and need no cumbersome clamps. The joints consist of a ground glass male joint (M) and a ground glass interior female joint (F) with exterior threads that allow the male portion to be secured by a septum-type plastic cap using an "O"-ring compression seal. (Cap and "O"-ring are included with all threaded male joints.) Most pieces have stopcock side arms which permit the evacuation of air and the introduction of an inert gas. A high vacuum is not necessary since the purge cycle is repeated a number of times. The versatility of Aldrich Schlenk-type glassware makes the manipulation of air- and moisture-sensitive reagents easier and safer.

Designed for small-scale manipulation of air- and moisture-sensitive reagents



**Addition of Liquids • Chemical Reaction
Distillation • Drying • Extraction
Filtration • Recrystallization
Degassing • Transfer of Solids**



For instructional videos on Schlenk-line techniques and dry box manipulations, see:
http://www.chem.cuhk.edu.hk/lab_technique_6handling.htm

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Schlenk Techniques

In order to avoid contamination by grease from tapered joints, use teflon sleeves or PTFE sealing rings. The latter, in particular, provide a faster, better fit than teflon tape and are more convenient than teflon sleeves.

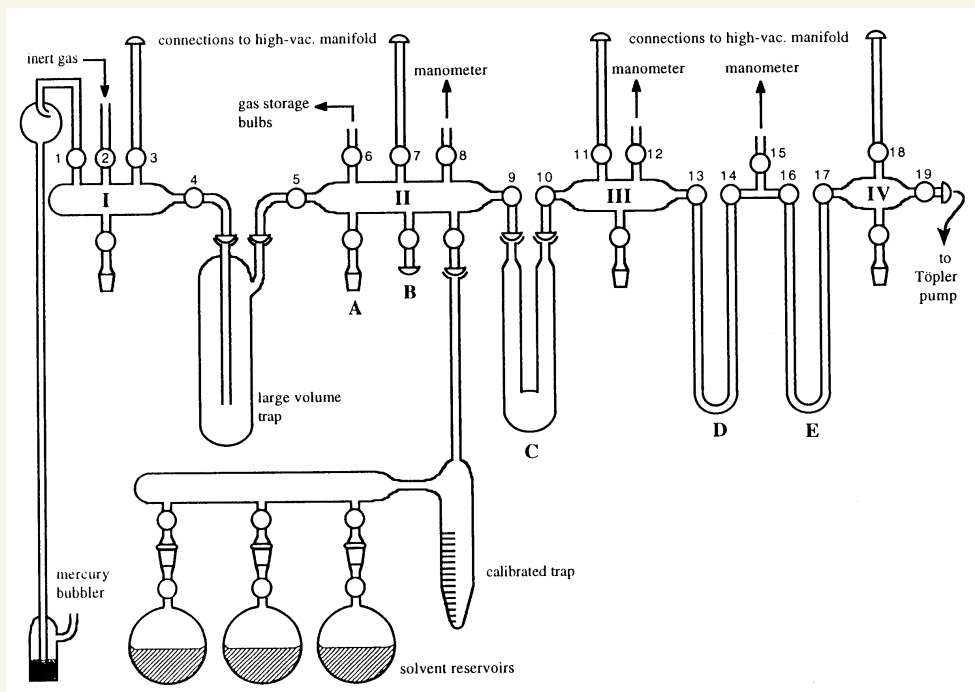


Glindemann PTFE Sealing Ring for Taper Joints



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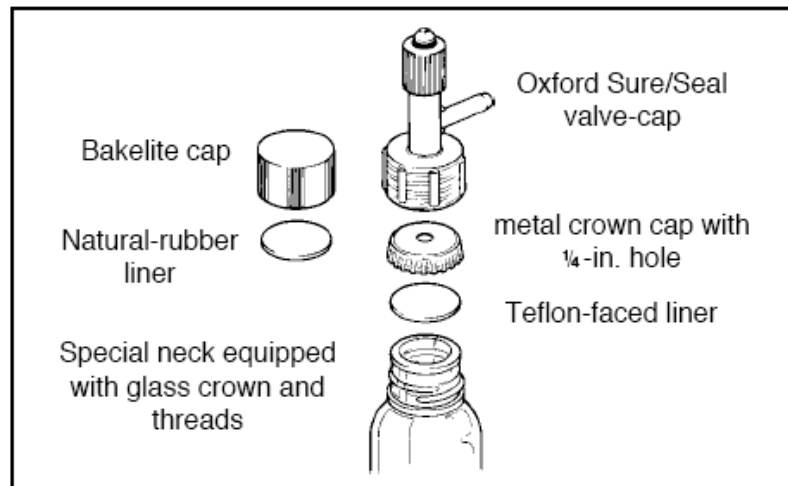
The Crown Jewel of Schlenk Techniques - The High Vacuum Line



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Storage

SURE/SEAL BOTTLE SYSTEM



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Storage

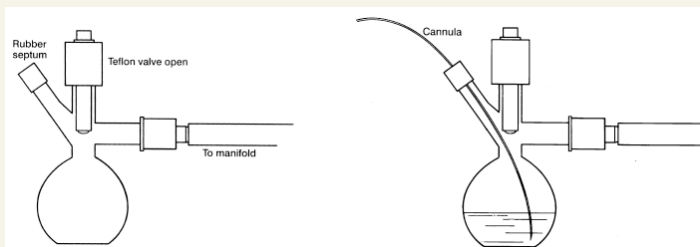
SURE/STOR FLASKS

Designed for safe, reliable storage and dispensing of air-sensitive and odoriferous chemicals, pyrophorics, alkyl lithiums, Grignards, corrosives, and purified or deuterated solvents.



Features:

- High-vacuum Teflon valve-to-glass seal eliminates air contamination in storage and septum leakage after initial needle penetration
- Heavy-wall borosilicate glass
- Removable sidearm hose connector for easy attachment of vacuum and inert gas lines. For long-term storage, replace hose connector with a rubber septum for secondary protection. Flasks supplied with 2 septa. Order replacement septa, Z10,649-6, below
- Plastic-coated* flasks reduce chance of breakage and contain spills
- Amber flasks protect light-sensitive products



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Gas Handling

You must be very careful not to let pressure build up in any piece of apparatus. Schlenk techniques can tolerate pressures only slightly greater 1 atm. If you have a pressure of 2 atm in a flask (twice the external pressure) that's 15 pounds on every square inch (psi) of your apparatus. So a stopper with a one square inch opening will have 14.7 pounds pushing it open. This is equivalent to hanging a bowling ball off of it! Be sure—whenever you work with gases—that you know what will happen anytime you open a valve, where the gas is supposed to be going, and where the gas will go if the pressure by accident gets too high.

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Gas Handling



For lecture bottles

Note: you will be expected to know—perhaps on the exam—
all the various pressure units used in this class:
 $1 \text{ atm} = 1.01 \text{ bar} = 14.7 \text{ psi} = 760 \text{ mm Hg} = \sim 33 \text{ ft or } \sim 400 \text{ in of water}$

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Safe Handling of Diazomethane



Diazald kit

The Diazald kit is a set of distillation glassware designed for the safe preparation of diazomethane (~100mmol). Glassware without sharp edges or ground-glass joints is recommended by de Boer and Backer (Org. Syn., Coll. Vol. 4 1963, 250). The Diazald kit features $\frac{1}{2}$ 19/22 Clear Seal joints; these joints do not require grease even for vacuum applications, thus avoiding that source of contamination. The glassware in the kit should be washed with care and without the use of wire brushes which will scratch the inner surface. For further information, request Technical Information Bulletin No. AL-180 and for a review on the preparation and reactions of diazomethane, see Aldrichim. Acta 1983, 16 (1), 3.

Cat.No. _____ Each
[Z10.025-0](#)

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Solvent Purification and Degassing

Methods of Degassing

• Freeze-Pump-Thaw

This is the most effective methods for solvent degassing. A solvent in a sealed Schlenk or heavy wall sealed tube is frozen by immersion of the flask in liquid N_2 . When the solvent is completely frozen, the flask is opened to the vacuum (high vacuum) and pumped 2-3 minutes, with the flask still immersed in liquid N_2 . The flask is then closed and warmed until the solvent has completely melted. This process is repeated (usually three times) and after the last cycle the flask is backfilled with an inert gas. Degassed solvent in a sealed Schlenk flask can usually be kept for 1-2 days.

• Atmosphere Exchange Under Sonication

Solvents can be roughly degassed by repeated sonication under light vacuum (i.e. house vacuum) for 0.5-1 min and replenishing the atmosphere with an inert solvent. By using 5-10 cycles, degassed solvents for HPLC and some reactions can be obtained quickly.

• Purging

Of the methods listed here, purging is the least effective way of degassing solvent, however it is acceptable for some applications, particularly when large amounts of solvent need to be roughly degassed. Purging consists of bubbling an inert gas (usually N_2 or Ar) through the solvent for 30 min - 1 hour. Care should be taken to prevent solvent evaporation and especially the condensation of water in the solvent by using an appropriate setup.

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Solvent Purification and Degassing



Effective but hazardous

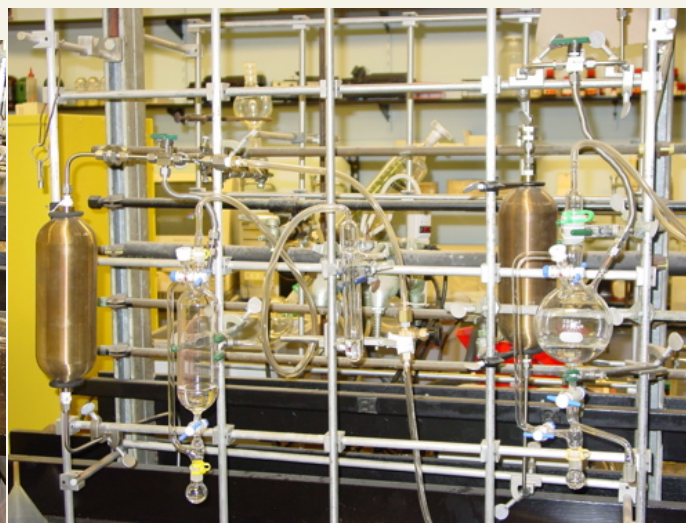
Considerably safer,
but still requires additional
precautions



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Solvent Purification and Degassing

By Filtration:



A simple setup from our labs.

See also: Alaimo, P. J.; Peters, D. W.; Arnold, J.; Bergman, R. G., "Suggested modifications to a distillation-free solvent purification system." *J. Chem. Ed.* **2001**, 78, 64.

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Solvent Purification and Degassing

A more elaborate, self-designed solvent filtration system from our labs.



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Further Reading

- Good references for the handling of air-sensitive compounds are the books
- The Manipulation of Air-Sensitive Compounds (2nd Ed.) by D. F. Shriver and M. A. Drezdson, Wiley-Interscience, New York, 1986.
- Advanced Practical Inorganic and Metalorganic Chemistry by R. J. Errington, Blackie, London, 1997.
- http://www.sigmaaldrich.com/etc/medialib/docs/Aldrich/Bulletin/altechbullal134.Par.0001.File.tmp/al_techbull_al134.pdf

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GUIDELINES FOR SAFE USE OF CHEMICAL SYRINGES

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Technical Bulletin AL-134

Handling Air-Sensitive Reagents

The Aldrich® Sure/Seal™ system

Anhydrous solvents and air-sensitive reagents from Aldrich are packaged in our exclusive Sure/Seal bottles which provide a convenient method for storing and dispensing research quantities of these products. With this bottle, reactive materials can be handled and stored without exposure to atmospheric moisture or oxygen. The reagent comes in contact only with glass and a specially designed resin layer, yet it can be readily transferred using standard syringe techniques.

The polypropylene cap on a Sure/Seal bottle can be safely removed because the crown cap and liner are already crimped in place. The reagent can then be dispensed using a syringe or double-tipped needle inserted through the hole in the metal cap (Fig. 1). We recommend only small-gauge needles (no larger than 18-gauge) be used and the polypropylene cap be replaced after each use. After the needle has been withdrawn from the bottle, the new elastomer liner provides outstanding resealing properties to protect the contents within from moisture and oxygen in the atmosphere.



Fig. 1 Crown cap with hole



Equipment Overview

Reactions involving our air-sensitive reagents can be carried out in common ground-glass apparatus. Other equipment required are a source of inert gas, a septum inlet, a bubbler, and syringes fitted with suitable needles.

Glassware preparation

Laboratory glassware contains a thin film of adsorbed moisture which can be easily removed by heating in an oven (125 °F/overnight or 140 °F/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.

Most of the techniques described in this bulletin were developed for handling various organoborane reagents. However, these methods are applicable to other air-sensitive solvents and reagents on a preparative laboratory scale.

Contents

- The Aldrich Sure/Seal™ system
- Equipment overview
- Reagent transfer with syringes
- Reagent transfer with double-tipped needles
- Storage vessels
- Equipment clean-up
- Labware for handling air-sensitive solvents and reagents
- Trademarks

Sigma brand products are sold through Sigma-Aldrich, Inc. Sigma-Aldrich, Inc. warrants that its products conform to the information contained in this and other Sigma-Aldrich publications. Purchaser must determine the suitability of the product(s) for their particular use. Additional terms and conditions may apply. Please see reverse side of the invoice or packing slip.

Inert gas supply and flushing equipment

Joint clips are required to secure joints during flushing since the nitrogen pressure may open the seals of unsecured standard-taper joints. Only high-purity, dry nitrogen from a cylinder with a pressure regulator (adjusted to 3-5 psi) should be used for flushing. Plastic tubing can be used to connect the nitrogen line to a tube connector (equipped with a stopcock) on the reaction apparatus. Nitrogen may also be introduced through a rubber septum via a hypodermic needle connected to the end of the flexible tubing on the nitrogen line. The needle-tubing connector provides a simple method for attaching the needle to the tubing. When not in use, this nitrogen-flushing needle should be closed by inserting the needle into a solid rubber stopper or septa to prevent diffusion of air into the needle when the nitrogen is turned off (Fig.2).

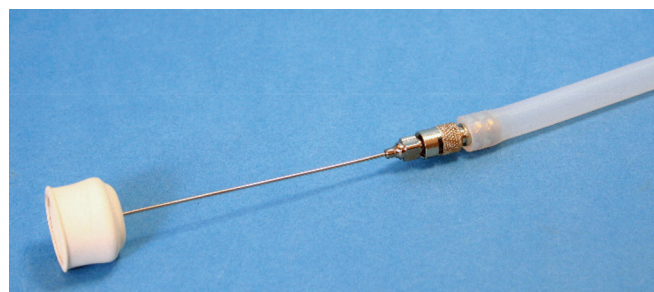


Fig. 2. Nitrogen-flushing needle

Septum inlet glassware

Large rubber septa may be used to cap female joints. However, the use of 6 mm septa and 9 mm o.d./6 mm i.d. medium-wall glass septum inlets is preferred. The small rubber septum provides a more positive reseat after puncture and allows less rubber to be in contact with organic vapors in the reaction vessel. With the recommended medium-wall tubing, the 6 mm septum not only fits the inside diameter of the glass tube but also fits snugly over the outside when the top is folded over (Fig. 3). The glass septum inlet can be built into the reaction flask (Fig. 4) or placed on an adapter (Fig. 5) for use with unmodified glassware. The rubber septum may be secured in place as shown in Fig. 3. with a nylon Wrap-it Tie. However, if the 6 mm septum is properly fitted to 9 mm medium-wall tubing, the ties may not be needed unless high pressures (>10 psi) are expected.

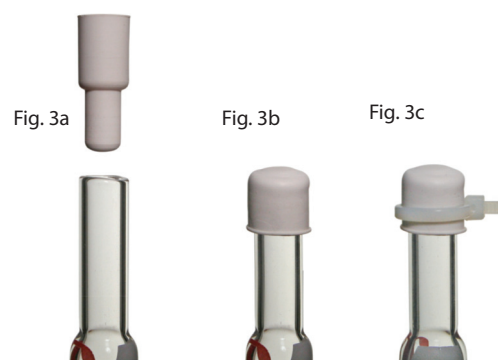


Fig. 3. Use of septum inlet

Fig. 4. Flask with septum inlet



Fig. 5. Septum inlet adapter



Bubblers for pressure equalization

To maintain an air-tight system the reaction vessel must be vented through a mercury or mineral oil bubbler. Drying tubes will not prevent oxygen from entering the system. At all times during the reaction, the system should be under a slight positive pressure of nitrogen as visually indicated by the bubbler. Fig. 6 illustrates a suitable bubbler. A pressure reversal may cause the liquid in the bubbler to be drawn into the reaction vessel. The enlarged head space in the bubbler will minimize this danger. However, if a large pressure reversal occurs, air will be admitted into the reaction vessel. The T-tube bubbler shown can be used to prevent this problem because nitrogen pressure can be introduced intermittently through the septum inlet. The problem can be completely eliminated by a slow and continuous nitrogen flow.

Syringe transfer tips

Small quantities (up to 50 mL) of air-sensitive reagents and dry solvents may be transferred with a syringe equipped with a 1-2 ft long needle. These needles are used to avoid having to tip reagent bottles and storage flasks. Tipping often causes the liquid to come in contact with the septum causing swelling and deterioration of the septa, and should therefore be avoided.

A rubber septum provides a positive seal for only a limited number of punctures depending on the needle size. Therefore, always reinsert the needle through the existing hole. It is also advantageous to put a layer of silicone or hydrocarbon grease on a rubber septum to facilitate passage of the needle through the rubber and to minimize the size of the hole in the septum.

Syringe/needle preparation

Ideally, the syringe and needle should be dried in an oven prior to use. Naturally, the syringe body and plunger should not be assembled before being placed in the oven. The syringe should be flushed with nitrogen during the cooling. A syringe may also be flushed 10 or more times with dry nitrogen (**Fig. 7**) to remove the air and most of the water adsorbed on the glass. A dry syringe may be closed to the atmosphere by inserting the tip of the needle into a rubber stopper or septa. (**Fig 2**). The syringe-needle assembly should be tested for leaks prior to use. The syringe is half-filled with nitrogen and the needle tip is inserted in a rubber stopper. It should be possible to compress the gas to half its original volume without any evidence of a leak. A small amount of stopcock grease or a drop of silicone oil placed on the Luer lock tip will help ensure tightness.

Reagent transfer with syringe

The syringe transfer of liquid reagents (up to 100 mL) is readily accomplished by first pressurizing the Sure/Seal™ reagent bottle with dry, high-purity nitrogen followed by filling the syringe (**Fig. 8**).

1. The nitrogen pressure is used to slowly fill the syringe with the desired volume plus a slight excess (to compensate for gas bubbles) of the reagent. Note the nitrogen pressure pushes the plunger back as the reagent enters the syringe. The plunger should not be pulled back since this tends to cause leaks and create gas bubbles.
2. The excess reagent along with any gas bubbles is forced back into the reagent bottle (**Fig. 9**).
3. The accurately measured volume of reagent in the syringe is quickly transferred to the reaction apparatus by puncturing a rubber septum on the reaction flask or addition funnel (**Fig. 10**).
Note: larger syringes are available but are awkward to handle when completely full.

Reagent transfer with a double-tipped needle

To conveniently transfer 50 mL or more of reagent, the double-tipped needle technique is recommended. **Fig. 11** illustrates liquid-reagent transfer under nitrogen pressure using this technique.

1. To accomplish the double-tipped needle transfer, the needle is first flushed with nitrogen.
2. The Sure/Seal bottle is pressurized with nitrogen using the nitrogen flushing needle.
3. The double-tipped needle is then inserted through the septum on the reagent bottle into the head space above the reagent. Nitrogen immediately passes through the needle. Finally, the



Fig. 6 Bubbler

Fig. 7 Flushing a syringe with nitrogen

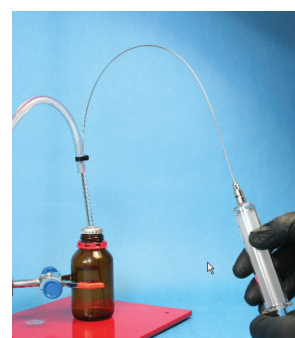
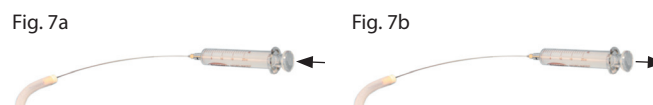


Fig. 8 Filling syringe using nitrogen pressure

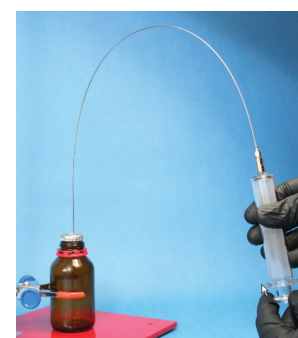


Fig. 9 Removing gas bubbles and returning excess reagent to the Sure/Seal bottle

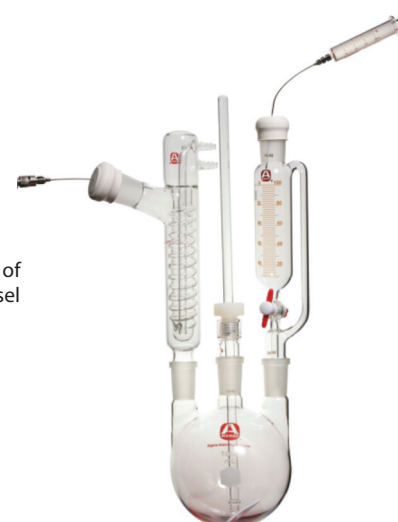


Fig. 10 Syringe transfer of reagent to reaction vessel

other end of the double-tipped needle is inserted through the septum on the reaction apparatus, and the end of the needle in the reagent bottle is pushed down into the liquid. The volume of liquid reagent transferred is measured by using a calibrated flask or addition funnel. When the desired volume has been transferred, the needle is immediately withdrawn to the head space above the liquid, flushed slightly with nitrogen, and removed. The needle is first removed from the reaction apparatus and then from the reagent bottle.

An alternative method

Transferring measured amounts of reagents (**Fig. 12**).

1. The reagent is first transferred via a double-ended needle from the Sure/Seal bottle to a dry, nitrogen-flushed graduated cylinder (**Fig. 13**) equipped with female joint and a double inlet adapter. Only the desired amount of reagent is transferred to the cylinder.
2. The needle is then removed from the Sure/Seal bottle and inserted through the septum on the reaction apparatus. By applying nitrogen pressure as before, the reagent is added to the reaction apparatus.

If it is necessary to add the reagent slowly, a modified transfer needle is constructed from two long standard needles and a male Luer lock to male Luer lock syringe valve. The valve may be opened slightly allowing only a very slow flow of reagent. Thus, the addition funnel is not needed and many reactions can be carried out in single-necked flasks (**Fig. 13**).

Storage vessels

The 12-gauge stainless steel needles on the Chem-Flex™ transfer line provide a rapid means of transferring air-sensitive reagents under nitrogen pressure. However, the needles are so large that once the crown cap liner on the Sure/Seal bottle is punctured, the liner may not self-seal. If only a portion of the contents is to be used, a needle no larger than 16-gauge should be utilized. By using small needles the reagent in a Sure/Seal bottle will not deteriorate even after numerous septum punctures.

However, if the reagent is to be used repeatedly for small scale reactions or if an unused portion is to be stored for an extended length of time, the material should be transferred from the Sure/Seal bottle to a suitable storage vessel.

One type of vessel is the Sure/Stor™ flask for air-sensitive reagents (**Fig. 14**). Alternatively, an appropriate adapter can be used to convert a round-bottomed flask into a storage vessel (**Fig. 15**).

The PTFE valve on the storage vessel keeps solvent vapors away from the septum, thereby minimizing swelling and deterioration of the septum. Furthermore, the valve allows for replacement of the septa. A change of septa is sometimes necessary because they tend to deteriorate on prolonged standing in a laboratory atmosphere.



Fig. 11 Double-tipped needle transfer of liquid reagent

Fig. 12 Double-tipped needle transfer to graduated cylinder

Fig. 13 Double-ended needle transfer with syringe valve



Fig. 14 Aldrich Sure/Stor™ flask



Fig. 15 Aldrich Sure/Stor™ adapter

Equipment cleanup

Clean-up of equipment that has been used to transfer air-sensitive reagents must not be taken lightly. Since many of these reagents react violently with water, fires are a potential hazard.

Empty Sure/Seal bottles – the crown cap and liner of an empty Sure/Seal bottle should be carefully removed and the open bottle left in the hood to allow the last traces of reactive reagent to be slowly air-hydrolyzed and oxidized. After at least a day, the inorganic residue can be rinsed out with water. Empty storage bottles and storage flasks should be treated similarly. Air-hydrolysis in a hood is appropriate only for the last traces of material that remain after a Sure/Seal bottle has been emptied as completely as possible via syringe or double-ended needle transfer. The Aldrich Catalog/Handbook or material safety data sheets should be consulted for the recommended disposal procedures for larger amounts of reactive chemicals.

Syringes and needles – Immediately clean all syringes and needles that have been used to transfer air-sensitive materials. Also, in general, a syringe should only be used for a single transfer. Failure to follow this practice can result in plugged needles and frozen syringes due to hydrolysis or oxidation of the reagents. The double-tipped needles are flushed free of reagent with nitrogen in the transfer system, and then immediately removed and placed in a clean sink. With water running in the sink and in the complete absence of flammable solvents and vapors, the double-tipped needles or Chem-Flex needle can be rinsed with water. When no activity in the rinse water is observed, acetone from a squeeze bottle can be flushed through the needle. Depending on the reagent transferred, it may be necessary to use dilute acid or base from a squeeze bottle to remove inorganic residue that is not water-soluble.

Following its use, a syringe contains a larger amount of residual reagent. It is advisable to rinse out the reactive reagent by first placing a few milliliters of the same solvent that was used for the reagent in a small Erlenmeyer flask in the hood. Keeping the needle tip under the solvent at all times, no more than half the solvent is then drawn into the syringe. The solvent plus dissolved residual reagent is ejected from the syringe back into the same Erlenmeyer flask. Repeat this rinse treatment at least three times. The wash solution can be safely combined with other waste solvents and

the syringe may be further cleaned with water and acetone in the sink. Again, treatment with dilute aqueous acid or base may be necessary.

Once the syringe needles and double-tipped needles have been rinsed in a sink, they can be further cleaned and dried using a device similar to that shown in **Fig. 16**. Needles are cleaned by inserting them through the septum. Vacuum from a water aspirator is used to pull solvents from squeeze bottles through the needles. After pulling air through the system for a few minutes, the syringe plus needle or double-tipped needle will be dry. The syringe plunger should be replaced in the barrel for storage. If a syringe plunger and barrel are not assembled for storage, dust can settle on the plunger and in the barrel. Upon reassembly, these fine particles will occasionally scratch the barrel or cause seizure of the plunger on the barrel. However, the plunger and barrel must be disassembled before oven drying.

Summary

When handling air-sensitive materials, be prepared for the unexpected. For example, at least one extra set of clean, dry syringes and needles or double-tipped needles should always be available in case the first set of equipment becomes plugged. When working with these air-sensitive reagents keep in mind that these solutions should never be allowed to come in contact with the atmosphere.

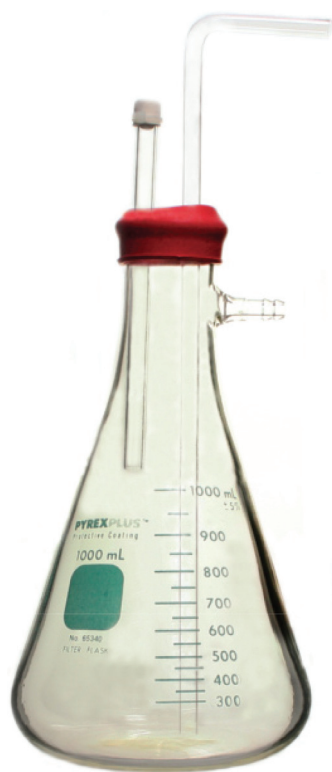


Fig. 16 Needle cleaning and drying technique

Labware for Handling Air-Sensitive Solvents and Reagents

A wide range of Labware products are available from Sigma-Aldrich for performing the techniques referenced in this technical bulletin. A sampling of these products are listed below. For additional products and ordering information, see the Sigma-Aldrich Labware Catalog or visit our website at sigma-aldrich.com/labware.

BUBBLERS

For safe pressure equalization during material transfers or reactions.

In-line bubbler

Use with oil or mercury, 5-7 mL. For monitoring gas evolution rate or rate of flow, or for closing off a reaction vessel from the atmosphere.

Cat. No. Z101214

In-line bubbler



SYRINGES, FITTINGS, AND NEEDLES

For transferring air-sensitive solvents and reagents.

Micro-Mate™ hypodermic syringes

Made from borosilicate glass with chrome-plated brass metal parts. Interchangeable barrels and plungers. All have needle-lock Luer tips. Additional sizes and tip styles are available.

Cat. No.	Capacity (mL)	Graduated (mL)
Z101052	5	0.2
Z101060	10	0.2
Z101079	20	1.0
Z101087	30	1.0
Z102342	50	2.0

Micro-Mate hypodermic syringes



All polypropylene Luer lock syringes

Non-contaminating, sterile, disposable syringes with safety stop to prevent plunger separation. Individually peel-packed.

Cat. No.	Capacity (mL)	Graduated (mL)
Z248002	3	0.1
Z248010	5	0.2
Z248029	10	0.5
Z248037	20	1.0

Polypropylene Luer lock syringes



Perfektum® one-way compression-nut stopcock

Additional stopcock types are available.

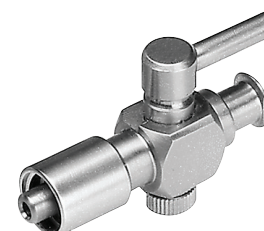
Female Luer to male Luer lock, not unidirectional.

Cat. No. Z102350

Male Luer lock to male Luer lock, not unidirectional.

Cat. No. Z102377

Perfektum one-way compression-nut stopcock (female to male)



Syringe needles with noncoring point

304 stainless steel, chrome-plated brass Luer hub, 18 gauge. Additional lengths and gauges are available.

Cat. No.	L (in.)
Z102717	6
Z117102	10
Z101141	12
Z100862	24

Stainless steel
304 syringe needles



Double-tipped transfer needles

304 stainless steel with a noncoring point on both ends. Additional lengths and gauges are available.

Cat. No.	L (in.)	Gauge
Z175595	12	20
Z101095	24	20
Z100889	24	18
Z100897	24	16
Z185221	24	14
Z185213	24	12
Z100900	36	16
Z185205	36	12

Double-tipped transfer needles

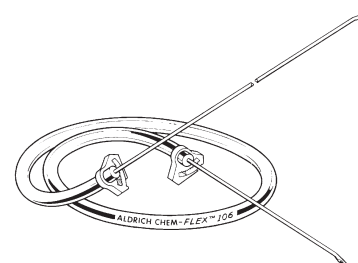


Chem-FLEX™ transfer lines

Two 12 gauge needles (6 and 18 in.) are connected to the Chem-FLEX 106 tubing with clamps. Liquids contact only PTFE and stainless steel during transfers.

Cat. No.	Tubing L (in.)
Z231029	30
Z281751	60
Z281778	120

Chem-FLEX transfer lines



INERT GAS SAFETY REGULATORS

For pressure transfer and purging operations.

The most compact laboratory regulator available. The bonnet is labeled "Inert Gas" to identify use. Outlet needle valve with ¼ inch NPTM connection. CGA 580 inlet.

Cat. No. Z569054

Inert gas regulator



RUBBER SEPTA

Additional septa sizes and types are available.

Red

Cat. No.	Size
Z565687	8 mm OD tubing
Z565709	9-10 mm OD tubing
Z554073	14/20 joints
Z554103	24/40 joints
Z554111	29/42 joints

White

Cat. No.	Size
Z565695	8 mm OD tubing
Z565717	9-10 mm OD tubing
Z553964	14/20 joints
Z553980	24/40 joints
Z553999	29/42 joints

Rubber septa



Reaction tube



SCHLENK TYPE GLASSWARE

Designed specifically for air-sensitive chemical reactions.

Reaction tubes

2 mm glass stopcock with 14/20 joint.

Cat. No.	Capacity (mL)
Z409235	10
Z409243	25
Z409251	50
Z409278	100
Z409286	250

Septum-inlet adapters



SEPTUM INLET ADAPTERS AND FLASKS

Small bore inlets for syringe transfers.

Septum-inlet adapters

Additional adapter styles are available.

Cat. No.	Stopcock	Joint
Z107387	Glass	14/20
Z107409	Glass	24/40
Z102288	PTFE	14/20
Z101370	PTFE	24/40

Septum-inlet flasks

Glass stopcock with 14/20 joint. Additional capacities and joint sizes are available.

Cat. No.	Capacity (mL)
Z515868	25
Z515876	50
Z515884	100
Z515914	250

Septum-inlet flasks



STORAGE BOTTLES AND FLASKS

For long-term storage of solvents and reagents.

Sure/Stor™ flasks

Designed for safe, reliable storage and dispensing of air-sensitive and odoriferous chemicals, pyrophorics, alkyl lithiums, Grignards, corrosives, and purified or deuterated solvents. High-vacuum PTFE valve. Additional flask sizes, amberized, and plastic-coated glass are available.

Cat. No.	Capacity (mL)
Z404977	25
Z404985	50
Z404993	100
Z405000	250

Sure/Stor flasks



Storage bottles

Clear glass with PTFE stopcock and septum inlets.

Cat. No.	Capacity (mL)
Z103284	125
Z103292	250
Z101990	500
Z102482	1,000
Z103306	2,000

Storage bottles





MATERIAL SAFETY DATA SHEET

Date of Issue: 13 March 2000
Revision: 5
ID: tmal

TRIMETHYLALUMINUM

1. IDENTIFICATION OF THE SUBSTANCE/PREPARATION AND COMPANY.

Product Name
Trimethylaluminum
Formula
(CH₃)₃Al
Company Identification
See footer.

2. COMPOSITION/INFORMATION ON INGREDIENTS

Substance/Preparation
Trimethylaluminum
Components/Impurities
None
EC No.
200-853-0
CAS No.
75-24-1

3. HAZARDS IDENTIFICATION

Pyrophoric liquid, decomposes violently in water. Skin contact can cause severe burns. Fumes may cause skin and eye irritation. Avoid inhalation of fumes.

4. FIRST AID MEASURES

Prompt medical attention is required in all cases of exposure to Trimethylaluminum and its by-products. Rescue personnel should be equipped with appropriate protective equipment (e.g. Self-contained breathing apparatus) to prevent unnecessary exposure and must be aware of the fire and explosion potential of Trimethylaluminum.

Skin

Contact may cause severe burns. Fumes may cause irritation. Immediately flush affected areas with large quantities of water. Remove affected clothing as rapidly as possible only if not stuck to skin.

Eyes

Contact may cause severe burns. Fumes may cause irritation. Persons with potential exposure to Trimethylaluminum should not wear contact lenses. Flush contaminated eyes with large quantities of water for at least 15 minutes. Hold eyelids open to ensure complete flushing.

Inhalation

May cause irritation. Move exposed personnel to an uncontaminated area quickly using self-contained breathing apparatus. If breathing is difficult, give oxygen. If breathing has stopped, apply artificial respiration. Medical assistance should be sought immediately. Keep victim warm and quiet.

5. FIRE-FIGHTING MEASURES

Extinguishing Media

Always use dry powder, soda ash or lime. Never use water, foam or halogenated compounds to fight fires involving organometallic materials. Without risk, stop flow of this compound to the fire. Without risk, and if safe to do so, move container(s) away from fire area.

Exposure Hazards

In a controlled fire any unreacted Trimethylaluminum may re-ignite when contact with air or water is renewed.

Special Protective Equipment for Fire-Fighters

Fire resistant clothing, self-contained breathing apparatus, face shield and safety goggles, safety shoes and fire resistant gloves.

6. ACCIDENTAL RELEASE MEASURES

Personal Precautions

Evacuate area. Use appropriate protective equipment. Purge equipment with inert gas before attempting repairs. Ensure adequate ventilation. If leak is in container call one of the emergency numbers as appropriate (See footer).

Environmental Precautions

Try to stop release, if safe to do so. For fire-fighting measures see Section 5.

Clean up method

Contact Epichem for specific advice.

7. HANDLING AND STORAGE

Handling

Valve outlet seals must remain in place unless container is secured and valve outlet piped to use point. Use a check valve or trap to prevent hazardous back flow into the container. Any equipment used for Trimethylaluminum service must be thoroughly cleaned and prepared to eliminate contamination and must be maintained in a leak-free state. All air and moisture in the system must be eliminated before use.

Storage

Protect containers from physical damage. Do not allow temperatures to exceed (125F) 51C. Store away from flammable material.

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

Exposure Controls

OSHA or ACGIH:

TLV= 2 mg/m³ (aluminum alkyls)
TLV(aluminum oxide)= 10 mg/m³
PEL(aluminum oxide)= 15 mg/m³ (ttl dust)
PEL(aluminum oxide)= 5 mg/m³ (resp. frac.)

OES and MEL: Long term exposure limit for aluminum alkyls:

2mg/m³ (8-hour TWA reference period).
Long term exposure limit for aluminum oxides:
(8-hour TWA reference period)

Total inhalable dust 10mg/m³

Respirable dust 5mg/m³

Ensure adequate ventilation.

Personal Protection

Self-contained breathing apparatus, fire resistant gloves, face shield and safety goggles, safety shoes, fire-resistant garments. Safety shower and eyewash.



9. PHYSICAL AND CHEMICAL PROPERTIES

Boiling Point: (261F)127C @ 760mmHg
Vapor Pressure: $\log_{10} P(\text{mmHg}) = 8.22 - 2134/T(\text{K})$
Freezing Point: (60F)15C
Liquid Density: 0.752g/ml @ 20C
Molecular Weight: 72.09 grams
Solubility in water: Reacts violently.
Appearance: Colorless liquid which is pyrophoric.

10. STABILITY AND REACTIVITY

Conditions to avoid

Reacts pyrophorically in air. It decomposes slowly above 100°C

Note: Trimethylaluminum is stable indefinitely in an inert atmosphere at room temperature.

Materials to avoid

Avoid water, air or other oxidizers.

Hazardous Decomposition Products

Aluminum Oxide dust, CO, CO₂

11. TOXICOLOGICAL INFORMATION

Aluminum Oxide dust formed when this compound is oxidized has caused toxic effects to the liver and kidneys in test animals. Exposure to aluminum oxide dust (which forms when trimethylaluminum burns) is not known to be acutely toxic.

Trimethylaluminum is not listed in the IARC, NTP or OSHA Subpart Z as a carcinogen or potential carcinogen.

Trimethylaluminum is listed on the TSCA inventory.

12. ECOLOGICAL INFORMATION

This product does not contain any Class I or Class II ozone depleting chemicals.

13. DISPOSAL CONSIDERATIONS

Regional and National regulations should be followed during waste disposal. Contact an Epichem representative for disposal of container and any unused quantities.

14. TRANSPORT INFORMATION

UN No: 3051
CLASS: 4.2 (4.3)
PG I
ECCN#: 3C003
IMDG Code: 4221
Shipping Name: Aluminum alkyls
(Trimethylaluminum)

15. REGULATORY INFORMATION

Classification

Highly Flammable, Corrosive

Risk and Safety Phrases

R14: Reacts violently with water.

R17: Spontaneously flammable in air.

R34: Causes burns.

S16: Keep away from sources of ignition – No smoking.

S43a: In case of fire use dry powder or lime - Never use water.

S45: In case of accident or if you feel unwell seek medical advice immediately. (Show label where possible)

16. OTHER INFORMATION

Ensure operators understand the pyrophoric and potentially thermally unstable nature of the product. DSC data available on request. Before using this product, it is recommended that a risk assessment and safety study be carried out. Further information on the use of this product can be obtained from the Technical Product Manager at the nearest Epichem facility.

SAFETY NOTICE: *In Order to provide our customers with the highest quality material and maintain our high standards of safety, the surface temperature of the bubbler will be monitored during the transportation of our products. We would like to monitor the surface temperature of the bubbler using a tempilabel. Tempilabel is a temperature-monitoring strip ranging from 120F to 150F (49C to 66C) which will indicate the temperature during shipment. The strip will turn black at one of the four ratings shown if the temperature is reached (normally a silver centre). If the temperature monitor is changed, please notify an Epichem representative immediately and we will assist you in the proper measures to be taken. We ask for your co-operation in our efforts of quality assurance and safety. If you have any questions or comments, please contact an Epichem representative. We thank you for your co-operation. Your assistance is greatly appreciated.*

Information contained in this material safety data sheet is offered without charge for use by technically qualified personnel at their discretion and risk. All statements, technical information and recommendations contained herein are based on tests and data which we believe to be reliable, but the accuracy or completeness thereof is not guaranteed no warranty of any kind is made with respect thereto. This information is not intended as a license to operate under or a recommendation to practice or infringe any patent of this Company or others covering any process, composition of matter or use.

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24 Hour Emergency Contact Numbers:

Europe: 44 151 334 2774 United States: Chemtrec: (800) 424 9300
Other International Countries: Chemtrec (703) 527 3887



Columbia University Environmental Health and Safety

The Safe Use of Pyrophoric Reagents

**Authored By: Kevin McGhee, EH&S
Professor Jack Norton, Dept. of Chemistry**

**Revised November 2009, March 2010
and May 2010**

Written April 2009

EXECUTIVE SUMMARY

November, 2009—Due to a recent incident involving the use of dry powder *sodium hydride*, EH&S has made some additions to this document to place greater emphasis on the use of solid pyrophorics. A brief section has been added before the techniques outlining the manipulation of liquid reagents to address issues concerning the use of metallic hydrides. All other material erstwhile contained herein is still held to be valid.

INTRODUCTION

In light of the recent fatal accident at UCLA, Columbia University EH&S has developed the following bulletin to serve as a guide for those who currently, or might in the future, use pyrophoric reagents. This guide is NOT to serve as a replacement for formal training in lab techniques or lab safety. Only qualified and experienced laboratory workers should ever attempt to manipulate these materials, and only after they have extensively researched and consulted knowledgeable peers with regard to the correct techniques for doing so. Failure to follow proper handling precautions can result in the exposure of these materials to the atmosphere, with consequences including serious injury or death.

Pyrophoric compounds are widely used in labs at Columbia. Here are some examples of the more common reagents:

- Organolithiums, such as t-Butyllithium
- Organozincs, such as diethylzinc
- Organomagnesiums (Grignard reagents)
- Aluminum alkyls, such as trimethyl aluminum
- Metallic hydrides, such as sodium hydride, potassium hydride, lithium aluminum hydride and some boranes.
- Finely divided metals, such as: aluminum, lithium, magnesium, titanium, zinc, zirconium, sodium, and potassium.

HAZARD INFORMATION

Pyrophoric reagents are extremely reactive to oxygen and moisture, and precautions must always be taken to prevent their exposure to air, which usually leads to spontaneous ignition. The danger of this reactivity is often exacerbated by the fact that these reagents are sold in solvents that are extremely flammable, such as ethyl ether, tetrahydrofuran (THF), or pentanes. When possible, compounds stored in pentanes or hexanes should be avoided, as storage in heptanes is *slightly* less hazardous.

The hazards from using these chemicals stem from fires that could result from the chemicals themselves and the solvents containing them, as well as any secondary fires that may spread to nearby flammable or combustible materials. Segregating combustible materials from storage as well as work areas is the best way to prevent dangerous secondary fires that could cause serious property damage and personal injury.

CONTROL MEASURES

Engineering Controls

- Solid pyrophorics must only be handled in an inert atmosphere glove box. Less expensive inert atmosphere glove bags are also available (<http://www.sigmaaldrich.com/labware/products/aldrich-atmosbag.html>).
- Pyrophoric liquids, or compounds dissolved in a liquid, should be stored in sealed containers with PTFE-lined septa to prevent air exposure.
- Handling of liquid pyrophorics must be conducted via cannula or syringe transfer to prevent exposure to air if not manipulated within an inert atmosphere (see below for more details).
- Manipulation of these reagents via syringe or cannula should always be conducted in a certified chemical fume hood, over a spill tray if possible, with the sash at the lowest practicable working height.
- Needles should be equipped with locking mechanisms to prevent accidental disconnection and release of reagents.
- Mineral oil bubblers must be employed at all times to release excess pressure from reagent or reaction vessels that can contribute to accidents. Balloons used for air-sensitive reagents are not suitable with pyrophorics.
- A blast shield is excellent, if available.

Administrative Controls/Safe Work Practices

- All users of pyrophoric reagents must first go through EH&S Lab Safety and Fire Safety training before working in a lab (<http://www.ehs.columbia.edu/Training.html>).
- Users must be trained thoroughly by a qualified and experienced supervisor on techniques for handling pyrophorics, and must be directly supervised when first starting with these techniques. It is best to try a few “dry runs” with the techniques using something less hazardous prior to using an actual pyrophoric material. Supervisors must also understand the hazards associated with these materials along with emergency response procedures, and relay this information to new users.

THE SAFE USE OF PYROPHORIC REAGENTS

Pyrophoric materials must only be used while other knowledgeable and experienced lab workers are present and aware of the procedure.

Pyrophoric materials must be used and stored away from all other flammable and combustible materials such as paper, bench liners, and solvents. Even open containers of water should be kept away due to the potential for a violent reaction.

Reagent bottles typically come in secondary containment within metal cans. If it is resealable, keep the manufacturer's can for storage of your reagents when not in use, and for disposal of the bottle after completion of the experiment involving the material. Otherwise, store in a clean, dry desiccator.

Highly flammable synthetic clothing is to be avoided, as well as loose clothing. Always wear long pants and closed-toe shoes in the lab. Tie back all loose hair to prevent ignition in the event of a flash fire.

Purchase only the smallest amounts necessary for your work, and discard old materials promptly. Reagents should be viewed with skepticism if older than six months, or if the septa have been pierced more than six times.

Personal Protective Equipment (PPE)

At a minimum, gloves, safety glasses, and a protective lab coat must be worn.

A lab coat made of fire resistant material, such as Nomex, is preferred to polyester or cotton.

It is recommended that you wear leather or Kevlar gloves beneath nitrile gloves for fire protection purposes.

Fully enclosed safety goggles or a face shield are preferred, if available, as they offer greater facial protection than safety glasses.

Emergency Preparedness and Response

Always know the exact location of your eyewash and shower and how to use all emergency equipment. Test your eyewash regularly. Keep the area around them clear from obstruction at all times.

It is best to choose the chemical fume hood closest to the safety shower to perform this work.

Users may encounter small fires at the tips of needles – know to expect this, and do not panic. A beaker of sand is useful for extinguishing this “pilot light”.

For skin exposures, if there are no severe burns, rinse with water for 15 minutes and seek first aid.

Keep a container of soda ash or sand within arm's reach in case a small fire occurs, as this can be safely used to smother the flames.

Class ABC dry chemical extinguishers can be safely used for most organometallic reagents that are dissolved in organic solvents, such as T-Butyllithium in heptanes.

For aluminum alkyl fires involving neat reagents, use MET-L-KYL® extinguishing powder, made by Ansul, Inc.

If you have access to Class D fire extinguishing material, know where it is and how to use it. Typically, Class D extinguishing material is used for large quantities of fires involving combustible metals. Contact EH&S at (212) 854-8749 (Morningside) or (212) 305-6780 (CUMC) to determine what type of extinguishing material is needed.

DO NOT use a CO₂ extinguisher to attempt to quench a fire with pyrophoric reagents – this can greatly exacerbate the problem.

Sodium Hydride (and other metallic hydrides)—Special Considerations

Sodium hydride is extremely reactive toward water, to the point that it will spontaneously react with moisture in air and ignite. As such, it should be treated with extreme caution as a solid pyrophoric material. It is strongly recommended that you substitute a mineral oil dispersion of sodium hydride for the “dry powder” form whenever possible. If this substitution cannot be made, “dry powder” sodium hydride, or any other metallic hydride such as lithium aluminum hydride or potassium hydride, must only be manipulated in an inert atmosphere, and must never be exposed to air. If a fire ever results during the use of a metallic hydride, use copious amounts of sand to smother the flames and the reagent. Never use an ABC fire extinguisher in an effort to put out a fire involving sodium hydride, as the force from the extinguisher can rapidly disperse fine powders.

TECHNIQUES FOR REAGENT TRANSFER

Equipment Preparation

Locate a needle of appropriate length and gauge. A sixteen-gauge needle is recommended if you plan to draw from the reagent container several times, as anything larger than this will leave a hole too large for the Teflon septum on the reagent bottle to reseal. A long needle is best if using a syringe. A long double-tipped flexible needle can be used for cannula transfer. Luer lock needles, or needles otherwise equipped with a locking mechanism, are highly recommended as a guard against the needles becoming detached.



Fig. 1 Drawing reagent into syringe from reagent container, with inert gas line inserted

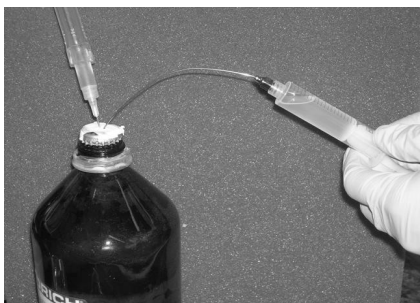


Fig. 2 Syringe is flipped needle-up after drawing liquid to allow inert gas bubbles to rise to needle



Fig 3. Inert gas bubbles and excess liquid are forced back into reagent bottle

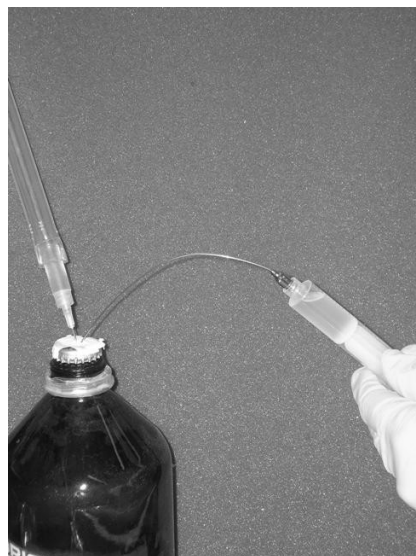


Fig. 4 Needle tip is brought into head-space of bottle, and an inert gas layer is drawn into syringe

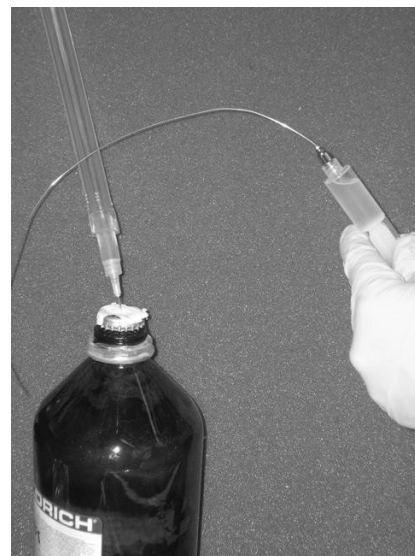


Fig. 5 Needle is carefully withdrawn from reagent bottle. Syringe is kept needle-up to prevent spilling

Flush your syringe-needle assembly, if using one, with dry, high-quality inert gas such as nitrogen or argon before starting. Ensure that it is leak-free by inserting the needle into a rubber stopper. You should be able to compress the syringe to half its original volume without any leaks. The needle can be left in the rubber stopper when not in use to prevent the entry of air.

Ensure that all glassware and other equipment involved in the procedure are clean and dry. Glassware should be heated in an oven to remove moisture, and cooled in an inert atmosphere.

Prepare an inert gas line for supplying positive pressure to the reagent container. Use a dry, high quality inert gas cylinder with a pressure regulator set to the lowest pressure sufficient for your work (no more than 5 psi), attached to flexible plastic tubing. A mineral oil bubbler should be added to the line, typically off of a manifold, to release excess pressure. A hypodermic needle at the end of the tubing can be used to insert the line through the septum of the reagent container. This needle can be inserted into a rubber stopper when not in use to prevent the entry of air.

The reaction vessel will also need to be supplied with a small amount of positive pressure during the reaction to prevent any pressure reversals that could cause air to enter the vessel. An inert gas line equipped with a mineral oil bubbler to relieve excess pressure will be needed for this. Run the reaction in a Schlenk flask that is under positive pressure from the inert gas line, connected via the tubing adapter. If the reaction vessel has a septum inlet, a hypodermic needle attached to the gas line can be pushed through the rubber septum to the reaction vessel, though the Schlenk vessel is better suited for controlling the atmosphere.

Syringe Transfer

Transfer of pyrophoric reagents via syringe is convenient, but should not be used for 20 mL or more.

Clamp your reagent container firmly. You will need a small amount of positive pressure in the reagent container in order to draw the reagent

into a syringe. Insert an inert gas line with low positive pressure (1-2 psi). Ensure that excess pressure is released through the mineral oil bubbler that is attached to the gas line. Simply sticking a needle through the septum, or using a balloon to relieve pressure, is not safe for pyrophoric reagents.

Prior to starting the procedure, ensure that the reaction vessel you plan to deposit your reagent into has a mineral oil bubbler to relieve pressure (if a bubbler is not already on the gas line), and that it is thoroughly flushed with inert gas prior to use. Again, do not use a balloon, and do not simply stick a needle through the septum to relieve pressure.

Before beginning, set aside an Erlenmeyer flask with the same solvent in which your reagent is dissolved. If it is a neat reagent, use a solvent that is inert and unreactive towards that reagent. Aliquot slightly more than the volume you will be transferring with the syringe. This flask will need to be immediately available after the transfer for flushing out your syringe.

Draw slightly more than you need initially. Be careful to pull only very gently on the plunger as pulling too strongly can cause leaks and create air bubbles. Always keep a good grip on BOTH the needle and the plunger to ensure that neither comes off. If the plunger is ejected with its contents due to excess pressure, you will have a dangerous fire on your hands. (Fig. 1)

Flip the syringe needle-up, so that the inert gas bubbles rise to the top (a long needle is needed for this). It is best to avoid allowing the reagent in the bottle to come into contact with the septum to prevent degradation. Tap the syringe a couple of times and look to make sure all the air/gas has been collected at the tip. (Fig. 2)

Push the plunger down to eject the inert gas and excess reagent back into the reagent vessel, stopping once the volume you need for your experiment is reached. (Fig. 3)

Pull the needle into the headspace of the reagent bottle and draw a small amount of inert gas into the syringe. This prevents spilling, and very importantly protects the liquid from exposure to air during transfer. (Fig. 4)

The needle can now be removed from the bottle, keeping the inert gas layer at the syringe tip. If you see a small flame at the tip of the needle, do not panic. You can use a beaker of sand to extinguish this. (Fig. 5)

Insert the syringe into the septum of the reaction vessel, keeping the inert gas layer between the syringe and needle, if you have a long needle. Ensure that the vessel is equipped with an inert gas line to provide positive pressure, and a mineral oil bubbler to relieve excess pressure. Holding the plunger down, inject the inert gas cushion in your reaction first, and then inject your liquid into the flask.

Cannula/Double-Tipped Needle Transfer

Transfer of pyrophoric reagents via cannula is recommended for 20 mL or more.

Clamp your reagent container firmly. You will need to create a small amount of positive pressure in the reagent container in order to force the reagent through your double-tipped needle. Connect it to an inert gas line to provide low positive pressure (1-2 psi). Ensure that the line is equipped with a mineral oil bubbler to relieve excess pressure. Using a balloon or simply sticking a needle through the septum to relieve pressure is not safe for pyrophoric reagents.

Make sure, before starting, that the reaction vessel into which you plan to deposit your reagent has a pressure release mechanism such as a mineral oil bubbler on the inert gas line, and that it is thoroughly flushed with inert gas prior to use. Again, do not use a balloon or simply stick a needle through the septum to relieve pressure.

Insert one end of the double-tipped needle into the headspace of the reagent vessel and allow the positive pressure from your inert gas line to flush the needle free of air.

Insert the other end of the double-tipped needle through the septum of the reaction vessel. To allow for a measured transfer, you can use a sealed, measured funnel attached to the reaction flask, with the septum at the top of the funnel.

When ready to transfer, push the needle that is in the headspace of the reagent container down into the liquid. The pressure from the inert gas line will begin forcing the liquid through the double-tipped needle.

When the desired volume has been transferred, pull the end of the needle in the reagent container up into the inert gas headspace and allow it to be flushed with inert gas again. Remove the end of the needle from the reaction flask first, and then from the reagent container. If, upon removal, a flame is lit at either tip, extinguish it in a beaker of sand.

Equipment Cleanup

If you use a syringe transfer, the syringe will have a small amount of the reagent remaining. Fill an Erlenmeyer flask with a small amount of the same solvent in which the reagent was stored, using slightly more than the volume which the syringe was used to transfer. If the syringe was used for a neat reagent, use a solvent that is inert and unreactive toward the reagent. Ensure that any flame at the tip of the needle is extinguished first, and put the tip of the needle beneath the liquid in the flask, keeping it beneath the solvent. Carefully draw the solvent into the syringe and eject it to flush the syringe, and repeat for a total of three rinses. Afterwards, the syringe can be disposed of by putting it into a sharps container, if it is disposable. The solvent in the flask, with trace amounts of the pyrophoric compound, should be added to your solvent waste container. Be sure to list all of the components on the chemical/hazardous waste label.

For a cannula transfer, the double-tipped needle should have been purged with inert gas before you removed it. The needle can be placed in a sink in the absence of any solvents or other combustible materials. Flush the needle with water, collecting the effluent for disposal with your aqueous waste. Making sure that there is no longer any reactivity, use a wash bottle to flush the needle with acetone, collecting the effluent with your solvent waste.

DISPOSAL

For any significant amount of reagent remaining in the reagent bottle, first ensure that the bottle is purged with inert gas. Place a secondary container such as a sealable plastic bag, or the manufacturer's can in which the bottle was shipped, into an inert atmosphere and purge it with inert gas. Put the reagent bottle into this purged secondary container and seal, then complete a chemical/hazardous waste label and submit an online chemical waste pickup request at <http://vesta.cumc.columbia.edu/ehs/wastepickup/>.

If only trace amounts of the reagent remain, use the solvent in which the reagent was originally stored to triple rinse the bottle (under positive pressure from an inert gas line when purging), collecting the rinse in your solvent waste container. If the bottle contained a neat reagent, perform this procedure with a solvent that is inert and unreactive toward the reagent. When finished, purge the bottle once more with inert gas and seal inside a secondary container, such as the metal can that came with the reagent. Complete the chemical/hazardous waste label and submit an online pickup request.

Sources

Aldrich Chemical Company, Inc.; *Handling Pyrophoric Reagents – Technical Bulletin AL-164*; May, 1995.

Aldrich Chemical Company, Inc.; *Handling Air-Sensitive Reagents – Technical Bulletin AL-134*; March, 1997.

Environmental Health and Safety, University of Nebraska at Lincoln; *Safe Operating Procedure – Pyrophoric Chemicals*; <http://ehs.unl.edu/sop/s-pyrophoric.pdf>; Revised July 2007.

Christensen, Kim; *Deadly UCLA Lab Fire Leaves Haunting Questions*; Los Angeles Times; March 1, 2009.

Department of Chemistry, University of Bath; *Risk Assessment – The use of small scale amounts of pyrophoric materials*; <http://www.bath.ac.uk/chemistry/safety/pyrophoric.html>; Revised November 18th, 2008.

Frontier, Alison, University of Rochester; *How to Syringe*; <http://chem.chem.rochester.edu/~nvd/howtosyringe.html>.

Thanks are due to Dr. Jack Norton, Professor of Chemistry at Columbia, Kathleen Kristian (his student) and Dr. Uttam Tambar.

Photos courtesy of Dr. Uttam Tambar.



The [Writing Safe Work Procedures Guideline \(OHS027\)](#) should be consulted to assist in the completion of this form

Faculty/Division: Faculty of Science		School/Unit: School of Chemistry		
Document number F10-SWP-374	Initial Issue date 29 th November 2011	Current version V1.3	Current Version Issue date 22 nd February 2012	Next review date 22 nd February 2014

2. Safe work procedure title and basic description of activity

Title: Storage, transport and use of pyrophoric organolithium reagents (incl. n-BuLi, t-BuLi)

Description of activity:-

Chemical synthesis involving use of an organolithium reagent)

3. List Hazards and risk controls as per risk assessment

Associated risk assessment number and location: F10-RA-374 See School of Chemistry Safety Page and Faculty of Science Database	Hazards:	Controls:
	Crack and broken glass	Inspect all glassware before handling – discard if faulty. Use appropriate PPE
	Flammable, toxic, and corrosive chemicals	Consult MSDS for all chemicals used and fill in the corresponding School of Chemistry Risk assessment form . Appropriate training. First aid on site. Wear proper PPE, especially protective eyewear and if possible, chemically compatible gloves. Dilute corrosive substances if possible. Avoid ignition sources. When possible, carry out all work in a fume hood. Clean up spillages immediately.
	Fire, Severe burns, Toxicity from the use of pyrophoric organolithium reagents	All work to be performed in a fume cupboard with a colleague trained in emergency procedures in attendance. Mandatory use of full face shield and fire resistant PPE. Proper mandatory training including background to use of pyrophoric materials and quiz, and practical demonstration
	Explosion of apparatus or reaction flask from the use of vacuum / inert gas under pressure.	Appropriate training and PPE. Consult also F10-SWP-174 on the use of vacuum and Schlenk lines.
	Sharp edges on needles, cannulas.	Appropriate training and PPE. Consult also F10-SWP-194 on the use of syringes.

Important Note: Organolithium reagents are pyrophoric – they may spontaneously ignite on contact with air! Improper – untrained – **use thus poses a serious threat** to the laboratory worker and laboratory, which includes serious fires **causing severe burns to, and even the death of, laboratory workers** and/or complete gutting of laboratories by fire.

Additionally organolithium compounds tend to be toxic and are commonly dissolved in flammable solvents that have their own associated hazards.

Other potential hazards associated with organolithium compounds include corrosivity, teratogenicity, water reactivity, and peroxide formation. Additionally, organolithium compounds can cause damage to the liver, kidneys, and central nervous system

Necessity for Use.

Use of organolithium reagents is, nevertheless, an important and irreplaceable methodology in chemical synthesis – both in the industrial setting and in the (academic) chemical research laboratory.

Organolithium reagents can be safely handled with adequate controls.

Controls.

1. **Mandatory training** (includes this SWP and RA-374) and **knowledge quiz prior to first use.**
2. All users must be directly supervised and trained in the use of the organolithium reagent by an experienced user until proficiency is demonstrated.
3. An up-to-date **Register of experienced users.** Only these users may use organolithium reagents.
4. **Mandatory use of proper fireproof personal protective clothing** (see section #4.)
5. All use of organolithium reagents must be performed in a **clean fumecupboard** that is vacant apart from a dual manifold (inert gas–vacuum) Schlenk line and the other equipment such glassware and magnetic stirrer associated with the experiment. An inert atmosphere glove box may also be used.
6. Minimising the amount of organolithium reagent used and ensuring proper controls for storage of organolithium reagents.

In the School of Chemistry, UNSW:

- to reduce risk, use the minimum concentration of organolithium reagent possible.
 - the maximum bottle size for an organolithium reagent is 100 mL.
 - larger bottles may only be purchased with the permission of the Head of School or the School Safety Committee.
 - a maximum volume of 100 mL of organolithium reagent may be used in any one experiment.
 - a single bottle of an organolithium reagent may be used a maximum of eight times (i.e. 16 piercings of the protective septum (see section 5)).
 - all bottles of organolithium reagents must be dated upon receipt and used or disposed within six months.
7. Organolithium reagents may not be used:
 - when alone
 - if possible, within 3 m of flammable solvents and reagents. At the very least, ensure there are no flammable solvents or reagents in the same fumehood or glovebox you are using.Another colleague trained in the use of fire extinguisher must be on hand at all times when organolithium reagents are used.
Flammable materials within the fumecupboard or glove box in which the organolithium is to be used must be removed before the organolithium is used. Ideally, although not always practical, no flammable materials should be within 3 m of the location where the procedure is to be carried out.
 8. A fire extinguisher must be at hand and a safety shower and eyewash must be available within 10 seconds travel time of where an organolithium reagent is used.
 9. Proper cleanup and disposal procedures.
 10. Providing disciplinary actions for workers not following safe procedures

4.List resources required including personal protective clothing, chemicals and equipment needed

SWP covers the storage, transfer and use of organolithium reagents including (but not necessarily limited to):

Alkyls –

Methyl-d3-lithium, as complex with lithium iodide solution 0.5 M in diethyl ether
Methylithium lithium bromide complex solution
Methylithium solution purum, ~5% in diethyl ether (~1.6M)
Methylithium solution purum, ~1 M in cumene/THF
Methylithium solution 3.0 M in diethoxymethane
Methylithium solution 1.6 M in diethyl ether
Ethyllithium solution 0.5 M in benzene/cyclohexane (9:1)
Isopropyllithium solution 0.7 M in pentane
Butyllithium solution 2.0 M in cyclohexane
Butyllithium solution purum, ~2.7 M in heptane
Butyllithium solution 10.0 M in hexanes
Butyllithium solution 2.5 M in hexanes

Butyllithium solution 1.6 M in hexanes
Butyllithium solution 2.0 M in pentane
Butyllithium solution ~1.6 M in hexanes
Butyllithium solution technical, ~2.5 M in toluene
Isobutyllithium solution technical, ~16% in heptane (~1.7 M)
sec-Butyllithium solution 1.4 M in cyclohexane
tert-Butyllithium solution purum, 1.6-3.2 M in heptane
tert-Butyllithium solution 1.7 M in pentane
(Trimethylsilyl)methylithium solution 1.0 M in pentane
(Trimethylsilyl)methylithium solution technical, ~1 M in pentane
Hexyllithium solution 2.3 M in hexane
2-(Ethylhexyl)lithium solution 30-35 wt. % in heptane

Alkynyls –

Lithium acetylide, ethylenediamine complex 90%
Lithium acetylide, ethylenediamine complex 25 wt. % slurry in toluene
Lithium (trimethylsilyl)acetylide solution 0.5 M in tetrahydrofuran
Lithium phenylacetylide solution 1.0 M in tetrahydrofuran

Aryls –

Phenyllithium solution 1.8 M in di-n-butyl ether

Others –

2-Thienyllithium solution 1.0 M in tetrahydrofuran
Lithium tetramethylcyclopentadienide
Lithium pentamethylcyclopentadienide

Laboratory equipment frequently used when undertaking reactions involving organolithium reagents includes:

Vacuum / Schlenk lines (see also F10-SWP-174)
Syringes and cannulae (see also F10-SWP-194)
Various glassware
Septa

Personal protective equipment (PPE):

All work with organolithium compounds must take place in a chemical fume-cupboard or inert atmosphere glovebox with the worker wearing the correct personal protective clothing



Clean, clear fume-cupboard fitted only with apparatus for the experiment to use the organolithium reagent.

This apparatus may include:

dual manifold (inert gas – vacuum) Schlenk line (see SWP174 and SWP173)
glassware

cannulae, syringes and needles, septa (see SWP194)
cooling baths and coolants (ideally, coolants should not be flammable); (see SWP151)
containment vessels/dishes
cleanup materials and spill kit
stirrer – heater (see SWP176)

All manipulations of organolithiums and other pyrophoric chemicals should occur in a clean, cleared fume cupboard with the **sash in the lowest feasible position**. Portable shields, which provide protection to all laboratory occupants, should be used where appropriate.

Personal protective equipment must include:

Eye and Face Protection

Chemical Splash goggles or safety glasses that meet AS/NZS standards must be worn whenever handling pyrophoric organolithium reagents. Ordinary prescription glasses will NOT provide adequate protection unless they also meet these standards.



A full face shield must also be worn.

Skin Protection

If possible, fire-resistant gloves must be worn when handling pyrophoric chemicals worn. Nomex® gloves are recommended with thin nitrile gloves under them. It is recognized here that it may be difficult to source gloves that are flexible/thin enough to use when working with syringes. If a user decides that the risk of mishandling a syringe while wearing thick gloves is more than the risk reduction offered by using fire-resistant gloves the user can proceed without using such gloves but with the uttermost care.



Nomex® fire-resistant gloves

Although the nitrile gloves are combustible, they provide an adequate secondary barrier (under the fire-resistant gloves) for handling most organolithium compounds in general laboratory settings.

A flame resistant laboratory coat or coveralls must be worn when using all organolithium and other pyrophoric reagents.

Flame resistant materials such as flame-retardant treated cotton and Nomex® provide thermal protection. They can ignite but will not continue to burn after the ignition source is removed. Flame resistance clothing should meet the appropriate AS/NZS standards (listed in section #9 below).



Lab coat made from NOMEX® IIIA

Clothing made of flammable synthetic materials including acetate, nylon, polyester, polypropylene, and spandex **must NOT be worn** when handling pyrophoric substances. Full-length trousers and a shirt with full length sleeves should be worn when handling pyrophoric reagents (this simple measure would have prevented the death of a researcher at UCLA due to burns received when using *tert*-butyl lithium).

Shoes must fully enclose the feet and should be impervious to solvent (e.g. be made of leather). No open toe shoes are allowed.

Eyewash and Safety Shower

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.

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

All persons handling organolithium reagents must know how to use this safety equipment.

5. List step by step instructions or order for undertaking the task

Researchers handling pyrophoric organolithium reagents in the laboratory must always be with a colleague trained in emergency response procedures.

In an emergency, your colleague must be available to assist should an accident occur.

Handling pyrophoric organolithium reagents –

Through use of proper syringe techniques, these reagents can be handled safely in the laboratory.

Use only clean, absolutely dry glassware, syringes, needles and cannulae.

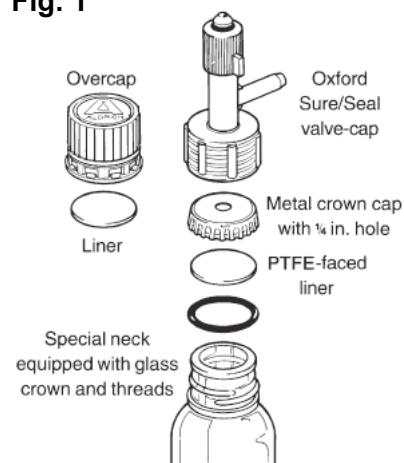
All apparatus that will come into contact with the organolithium reagent should be thoroughly cleaned and completely dried overnight in an oven held at over 110 °C.

The Aldrich Sure/Seal™ Packaging System

Use of the Aldrich Sure/Seal packaging system for organolithium reagents is recommended.

The Sure/Seal packaging system (**Fig. 1**) provides a convenient method for storing and dispensing air-sensitive reagents. Use of 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 medium-term storage.

Fig. 1



In the School of Chemistry, UNSW:

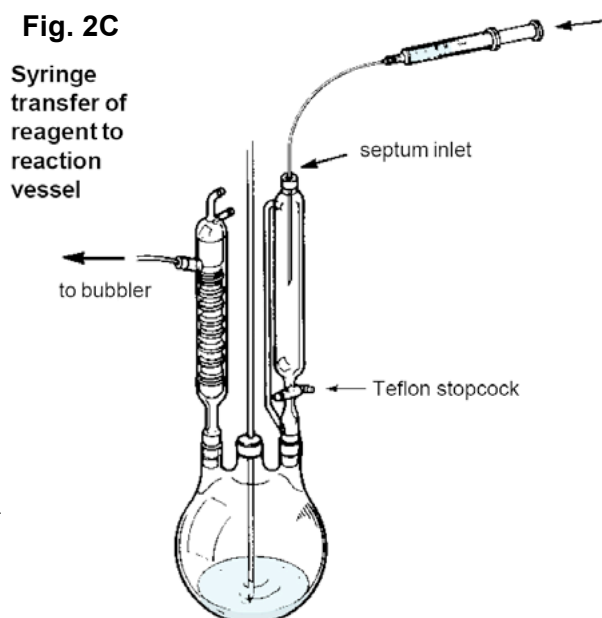
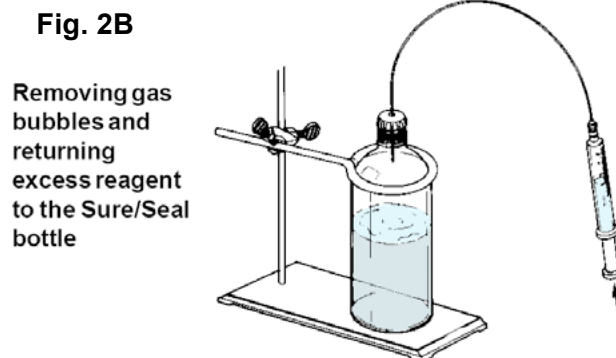
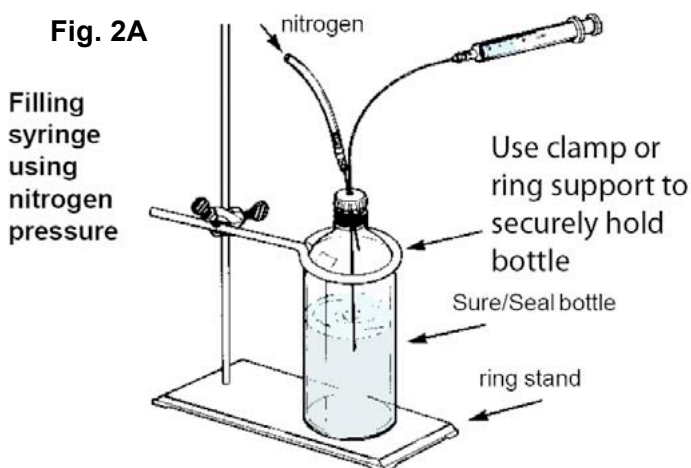
- **the maximum bottle size for an organolithium reagent is 100 mL, unless special permission is obtained.**
- **a maximum volume of 100 mL of organolithium reagent may be used** in any one experiment.
- **a single bottle of an organolithium reagent may be used a maximum of eight times** (i.e. 16 piercings of the protective septum); left-over or out-of-date reagent should be returned to the Chemistry Store for disposal as Hazardous Waste.

• **tall bottles of organolithium reagents must be dated upon receipt and disposed of whether they have been opened or are still unopened, six months from receipt.** It is strongly recommended that **opened bottles are disposed of with in within one month of first opening** (and no longer than six months) to prevent accumulation of explosive peroxides.

Luer syringes with glass barrels and pistons are adequate for most purposes, however some leakage can occur between the barrel and the piston, and with air-sensitive reagents this can cause the piston to stick. This represents a serious hazard since there is no easy way of emptying the syringe of residual liquid. In such cases, it is preferable to use a glass gas-tight syringe that has a metal or plastic piston with a Teflon tip. Syringes should only be used to dispense small volumes of reagents (up to 20 mL). Do not fill the syringe more than 60% full to minimize the possibility of accidentally pulling the plunger out of the syringe body.

Transferring Pyrophoric Reagents with Syringe

- In a fume cupboard (or inert atmosphere 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 20 mL) as shown in **Fig. 2A**. Pulling the plunger causes gas bubbles.
- 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**.
- 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 as illustrated in **Fig. 2C**.



Transferring Pyrophoric Reagents with a Double-Tipped Needle

- The double-tipped needle technique is recommended when transferring larger volumes of reagents (20 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. 3A

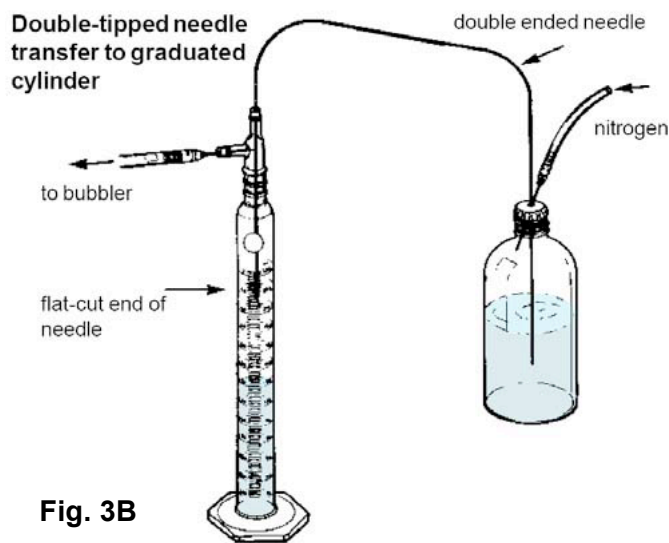
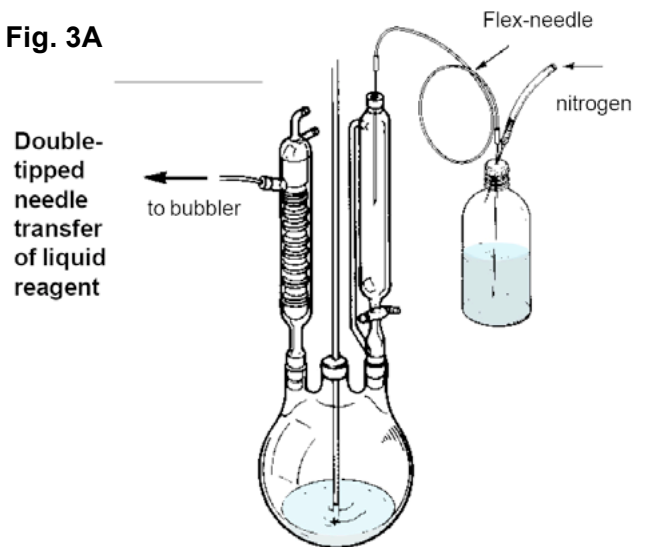
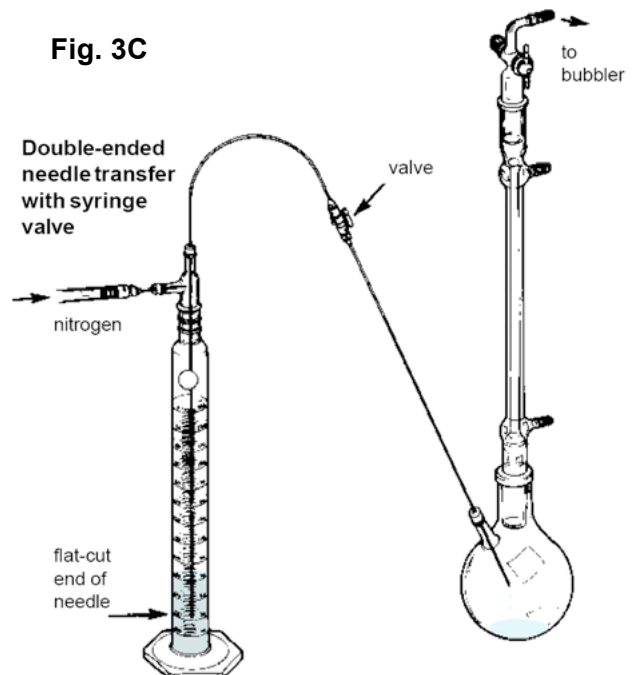


Fig. 3B

Fig. 3C



Cleaning syringes, needles and cannulae after use

- Immediately* after use, 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

- Organolithium reagents should be stored under an atmosphere of inert gas. Secondary containment is recommended.
- Areas with heat/flames, oxidizers, and water sources should always be avoided when handling organolithium reagents and are not appropriate as storage areas.
- Containers must be clearly labeled with the correct chemical name, hazard warning, date received, and with details of use including date and volume used.
- For extra protection after initial opening an use of a Sure/Seal bottle containing an organolithium reagent:
 - Close the overcap tightly.
 - Use parafilm around the overcap to provide additional protection from air and moisture.
 - Record the date and volume of reagent used on the bottle.



Reagent bottles must be dated when first opened so you will know when to dispose of them

DO NOT USE an organolithium reagent if
• the unopened or opened bottle is over six months old or
• the bottle has already been used eight times.

Such bottles should be disposed as Hazardous Waste.

It is recommended that opened bottles are not kept for more than one month even if they have been used less than eight times.

Transport

ALWAYS transport an organolithium reagent in a fireproof secondary container when taking it to another lab or through public spaces



Transporting a reagent bottle in secondary containment

6.List emergency shutdown procedures

- Shut off all ignition sources.
- Allow the spilled material to react with atmospheric moisture.
- Use powdered lime (CaO) to completely smother and to cover any spill that occurs. Keep containers of powdered lime and sand within arm's length when working with an organolithium reagent. Use sand to extinguish any small flame spouting from a needle that has been used to transfer an organolithium reagent.
- 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.
- Consider purchasing a fire blanket and keeping it near the working area to quickly extinguish flames on a person.
- In the event of skin contact, immediately wash with soap and water and remove contaminated clothing.
- In case of eye contact, promptly wash with copious amounts of water for 15 min (lifting upper and lower lids occasionally) and obtain medical attention.
- If pyrophoric material/solution is ingested, obtain medical attention immediately.
- If large amounts are inhaled, move person to fresh air and seek medical attention at once.
- **Raise the alarm: Call 9385 6666 and/or push the Break Glass Alarm** as appropriate.
- Respiratory protection maybe necessary in the event of a large spill or release in a confined area.

7. List Emergency procedures for how to deal with fires, spills or exposure to hazardous substances

Fires.

R escue people	from immediate danger, if safe to do so
A larm	raise the alarm; push break-glass alarm; call 9385 6666
C ontain fire and smoke	close all doors and windows, shut off the fume-cupboard and adjacent fume-cupboards, if safe to do so
E xtinguish	only attempt to extinguish fire by using appropriate fire-fighting equipment, if trained and safe to do so

Additional fire information:

Users may encounter small fires at the tips of needles – know to expect this, and do not panic. A beaker of sand is useful for extinguishing this “pilot light”.

DO NOT use a CO₂ or H₂O extinguisher to attempt to quench a fire with pyrophoric reagents – this can greatly exacerbate the problem.

Spills.

Procedures are covered in section #6 above. For major spills, Security must be contacted on 9385 6666.

Medical emergencies.

Call 9385 6666 immediately if a laboratory worker is injured and requires medical attention when using an organolithium reagent.

For skin exposures, if there are no severe burns, rinse with water for 15 minutes and seek first aid.

8. List Clean up and waste disposal requirements

Disposal of Pyrophoric Organolithium Reagents

- A container with any residue of pyrophoric organolithium reagents should never be left open to the atmosphere.
- Residues of organolithium compounds can be safely quenched under an inert atmosphere by diluting to less than 5 wt.% with an inert solvent such as heptane (avoid using solvents with low flash points such as pentane or diethyl ether). This solution is then slowly added to a well-stirred 2M solution of 2-propanol in heptane under an inert atmosphere, while maintaining the temperature below 50°C. The resultant solution of lithium iso-propoxide is then quenched by careful addition of methanol, then excess water.
- The essentially empty container should then be rinsed three times with an inert dry solvent such as dry toluene and heptane; this rinse solvent must also be hydrolyzed or neutralized prior to disposal as waste.
- After the container is triple-rinsed, it should be left open in back of a hood or atmosphere at a safe location for at least a week. After the week, the container should then be rinsed 3 times again.

Dispose of other solvents, dirty oil, etc. in the proper waste drum according to the School of Chemistry procedures (see e.g., F10-SWP-411).

9. List legislation used in the development of this SWP

NSW OHS Act 2000, NSW OHS Regulation 2001, Code of Practice for the Labelling of Workplace Substances AS/NZS 2243.2:2006. Safety in laboratories. Part 2: Chemical aspects
AS/NZS 2243.6-1990. Safety in laboratories. Part 6: Mechanical Aspects.
AS/NZS 2243.3:2006 Safety in Laboratories Part 7 Electrical aspects
AS/NZS 2161.1:2000 Occupational Protective Gloves – Selection, Use and Maintenance
AS 2374:1980 - Guide to the selection, care and use of clothing for protection against heat and fire.
AS/NZS 4502.1-3:1997 - Methods for evaluating clothing against heat and fire

Other sources and additional information:

Created from a variety of resources, principally the Sigma-Aldrich Technical Bulletins, the Online Training in Organolithium Use at Yale University and these websites and articles:

<http://www.chemistry.ucla.edu/file-storage/publicview/pdfs/SOPLiquidReagents.pdf>

www.safety.rochester.edu/ih/standops8.html

www.brandeis.edu/ehs/labs/pyrophoric.html

<http://ehs.columbia.edu/pyrophorics.pdf>

<http://www.yale.edu/ehs/onlinetraining/OrganoLithium/OrganoLithium.htm>

Safe handling of organolithium compounds in the laboratory, J. A. Schwinderman, C. J. Woltermann and R. J. Letchford, *Chemical Health and Safety*, May/June 2002, 6-11.

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>

For further reading on syringe and cannula techniques, see:

Advanced practical inorganic and metalorganic chemistry, R. J. Errington, 1997, Chapman & Hall, London.

The manipulation of air sensitive compounds, D. F. Shriver, 1986, 2nd Ed, John Wiley and Sons, Chichester.

See also:

UNSW Emergency Procedures

Researcher Dies after Fire: <http://pubs.acs.org/cen/news/87/i04/8704news1.html>

California Inspectors Fine UCLA Lab in Fatal Fire:

<http://news.sciencemag.org/scienceinsider/2009/05/california-insp.htm>

10a. List competency required – qualifications, certificates, licensing, training - e.g. course or instruction:

Only registered approved experienced users may conduct experiments with pyrophoric organolithium reagents in the School of Chemistry, UNSW.

Prior to using organolithium reagents, all prospective users of organolithium reagents should read this SWP and RA-374 and they must complete a short online training video available from Yale University:

<http://www.yale.edu/ehs/onlinetraining/OrganoLithium/OrganoLithium.htm>

To ensure prospective user understands this SWP, RA-374 and the online training provided by Yale University, prospective users must complete a multiple choice quiz that can be obtained from the Head of School of Chemistry OHS committee.

Before using an organolithium reagent, a short quiz should be performed

New users of pyrophoric organolithium reagents must be directly supervised and trained in the use of the organolithium reagent by an approved experienced user until proficiency is demonstrated.

A School Register of Approved Experienced Users of Pyrophoric Organolithium Reagents is kept.

