ALDRICH®
Advancing Science
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6000 N. Teutonia Ave., Milwaukee, WI 53209
Telephone: (800) 558-9160 • (414) 438-3850
Fax: (800) 962-9591 • (414) 438-4234
Web site: sigma-aldrich.com
E-mail: aldrich@sial.com

AL-134 Technical Bulletin

Handling and Storage of Air-Sensitive Reagents

A variety of air-sensitive reagents are available from Sigma-Aldrich. Since these reagents react with water, oxygen, or both, they must never be exposed to the atmosphere. The remarkable chemistry of these reagents can be handled easily on a laboratory scale using syringe techniques. This data sheet is limited to those techniques necessary for handling air-sensitive reagents on a preparative laboratory scale.

The Aldrich Sure/Seal™ Packaging System

The exclusive Sure/Seal packaging system provides a convenient method for storing and dispensing research quantities of air-sensitive reagents. The plastic cap on a Sure/Seal bottle can be safely removed because the crown cap, with its PTFE/elastomer liner, is already crimped in place **Fig.1.** The reagent can then be dispensed using a syringe or double-tipped needle (16 gauge or less) inserted through the hole in the metal cap. Upon withdrawal of the needle, the small hole that remains in the PTFE/elastomer liner will not cause the reagent to deteriorate under normal circumstances. However, we recommend that the plastic cap be replaced after each use and in particular for long-term storage.

A Sure/Seal septum-inlet transfer adapter may also be used when repeated dispensing is necessary. This adapter protects the contents of the bottles from air and moisture. **Fig. 1B**

For extended storage of unused reagents use the solid plastic cap, or equip the bottle with an Oxford Sure/Seal valve cap **Fig.1**, or transfer the reagent to a suitable storage vessel.

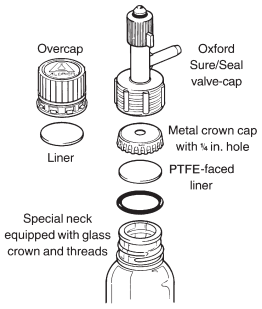


Fig. 1

Equipment

Reactions involving our air-sensitive reagents can be carried out in common ground glass apparatus or in greaseless, Schlenk-type glassware (see listings in Aldrich Handbook). Glassware normally contains a thin film of absorbed moisture that can be thoroughly removed by heating in an oven (125˚F overnight or 140˚F /4h). The hot glassware should be cooled in an inert atmosphere by assembling the glassware while hot and flushing it with 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. Spring clips or rubber bands are required to secure joints during flushing, since the nitrogen pressure may open the seals of unsecured standard taper joints.

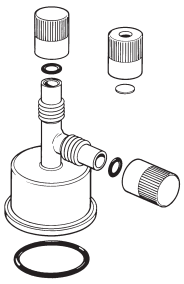


Fig. 1B

3-5psi high-purity dry nitrogen should be used for flushing. Plastic tubing with adapters may be used to connect the nitrogen (equipped with a stopcock) to the reaction apparatus. Nitrogen can also be introduced via a hypodermic needle through a rubber septum. After use, close the needle by inserting it in a rubber stopper to keep air out when the nitrogen is turned off **Fig. 2.**

Small rubber septa provide a positive reseal after puncture and allow less rubber to be in contact with organic vapors in the reaction vessel. A properly sized septum not only fits the inside diameter of the glass **Fig. 3**, but also fits snuggly over the outside when the top is folded over. A glass septum-inlet can be part of the reaction flask **Fig. 4** or placed on an adapter **Fig. 5.** The rubber septum may be wired in place as shown in **Fig. 3**.

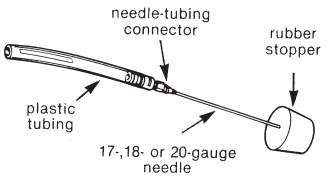


Fig. 2. Nitrogen-flushing needle

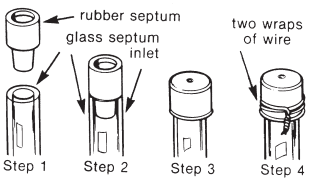


Fig. 3. Use of septum-inlet

Fig. 4. Flask with septum-inlet

Fig. 5. Septum-inlet adapter

During an airtight reaction, the system should be under a slight positive pressure of nitrogen as visually indicated by venting through a mineral oil bubbler **Fig. 6**.

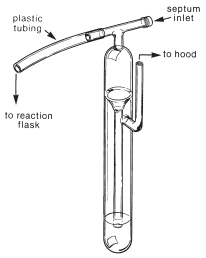


Fig. 6. Bubbler

The threat of a pressure reversal can be eliminated with a slow and continuous nitrogen flow introduced through the T tube septum inlet shown.

Small quantities (up to 50mL) of air-sensitive reagents may be transferred via syringe with a 1-2ft long needle. These needles avoid having to tip bottles, which reduces septa contact with the liquid.

When inserting a needle through a septum, a layer of silicone or hydrocarbon grease on the septum will help facilitate passage. When re-inserting a needle, always use an existing hole. Prior to use, the syringe should be disassembled and dried in an oven, flushed with nitrogen while cooling, and then closed to the atmosphere by inserting the tip of the needle into a rubber stopper. Test the syringe assemblies prior to use with the needle tip in a rubber stopper and the syringe half filled with nitrogen. There should be no evidence of a leak when compressed to its original volume. A little grease or silicone oil on the Luer lock helps.

Reagent Transfer with Syringe

Nitrogen pressure within a Sure/Seal bottle is used to slowly fill the syringe (up to 100mL) as shown in **Fig. 7**. 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. 8**. The desired volume of reagent in the syringe is quickly transferred to the reaction apparatus by puncturing a rubber septum as illustrated in **Fig. 9**.

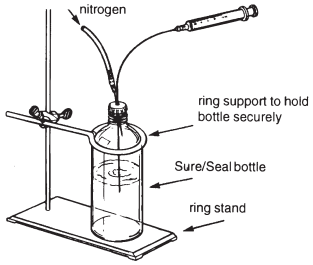


Fig. 7. Filling syringe using nitrogen pressure

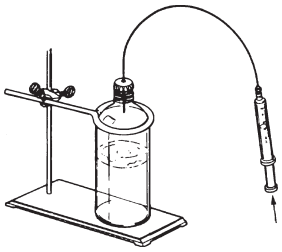


Fig. 8. Removing gas bubbles and returning excess reagent to the Sure/Seal bottle

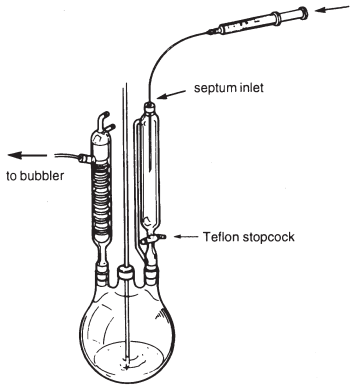


Fig. 9. Syringe transfer of reagent to reaction vessel

Reagent Transfer with a Double-tipped Needle

To transfer 50mL or more, the double-tipped needle technique is recommended. 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.

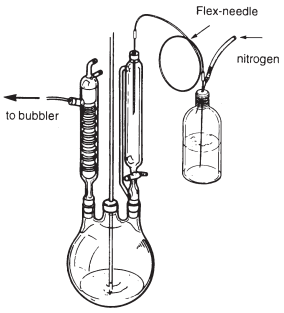


Fig. 10. Double-tipped needle transfer of liquid reagent

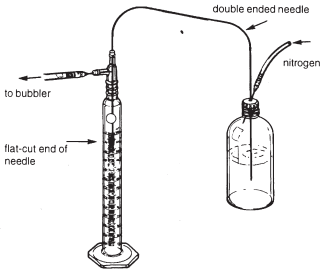


Fig. 11. Double-tipped needle transfer to graduated cylinder

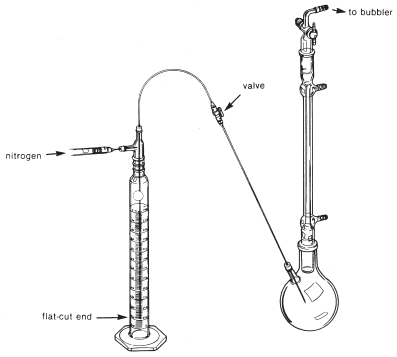


Fig. 12. Double-ended needle transfer with syringe valve

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. 11**. 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. 12**.

Storage Vessels

For extended storage of air-sensitive reagents, one type of container is shown in **Fig. 13**. Alternatively, an inlet adapter can be used to convert a round-bottom flask into a storage vessel. The PTFE valve on the storage flask keeps solvent vapors away from the septum, thereby minimizing septum deterioration. Further, the stopcock allows for the replacement of the septa.

PTFE will cold flow (creep) with time. Therefore, unattended long-term storage of a tightened PTFE stopcock or valve is not recommended. The valve should be turned occasionally (at least once a month) to check for tightness of its seal.

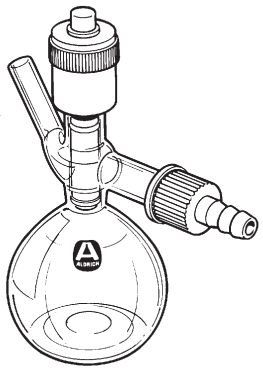


Fig. 13. Sure/Stor flask

Cold Storage

Due to the different thermal expansion coefficients of PTFE and glass, the PTFE plug in a glass barrel will leak when moved from room temperature to cold storage. The PTFE plug can be retightened after about 15 minutes in the cold room. Thereafter, open and close the stopcock only in the cold room. Conversely, glass breakage can occur when moving the flask from the coldroom to room temperature due to the expansion of the PTFE material. Do not attempt to turn an unattended stopcock after it has warmed to room temperature. To prevent breakage, turn the stopcock as the apparatus warms.

An all glass stopcock is an option. However, solvents used for our reagents will slowly dissolve most stopcock greases. When this is a concern, a PTFE-clad stopcock may be substituted. Given the expense and the limited lifetime of a PTFE-clad glass plug, it may be best to wrap the glass plug with PTFE tape. The tape must not be overlapped. A counterclockwise wrap will tighten when turned clockwise. When secured in place with a rubber band, the vessel can be stored for months in a cold room or at room temperature without any leakage or freezing of the stopcock.

Equipment Cleanup

Cleanup 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. The crown cap and liner of an empty Sure/Seal bottle should be carefully removed and the open bottle (or storage flask) 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. 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 Handbook or MSDS should be consulted for disposal procedures of larger amounts of reactive chemicals.

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.

A syringe contains larger amounts of residual reagent. Rinse out the reactive agent 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 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 rinsed the syringe needles and double-tipped needles can be further cleaned and dried using a device as shown in **Fig. 14**. 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 the double-tipped needle will be dry. The syringe plunger should be replaced in the barrel for storage to prevent dust contamination. However, the plunger and barrel must be disassembled before oven drying.

Most of the above techniques were developed for handling various organoborane reagents. However, these methods are applicable to other air-sensitive materials. 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.

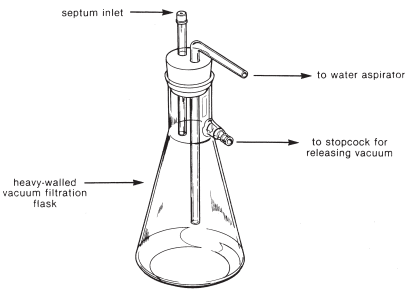


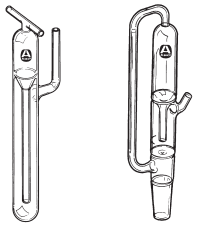
Fig. 14. Needle cleaning and drying technique

Bubblers

A. B. Aldrich bubblers

Mineral oil or mercury, 5 to 7mL. For monitoring gas evolution or flow rate, or closing off a reaction vessel from the atmosphere. Model B has a ⅀24/40 joint.

A. Z10121-4 B. Z10432-9

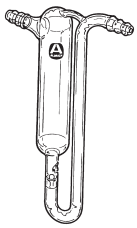


A B

C. Aldrich 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.

Description	Cat. No.
Single inlet tube, top outlet (shown)	**Z22501-0**
T inlet tube, side outlet	**Z22502-9**

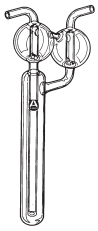


C

D. Aldrich safety bubbler

Unique design, with 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.

Z22372-7

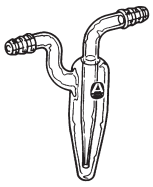


D

E. Aldrich mini gas bubbler

For bubble counting.
Maximum volume is 4mL.

Z22371-9

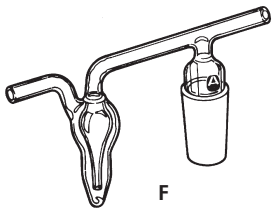


E

F. Aldrich in-line oil bubblers

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

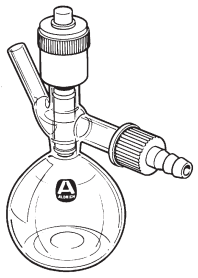
⅀ Joint	Cat. No.
14/20	**Z22322-0**
19/38	**Z22334-4**
24/40	**Z22335-2**



F

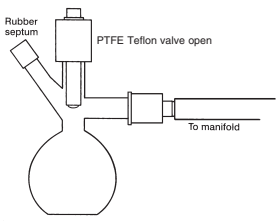
Aldrich Sure/Stor™ Flasks

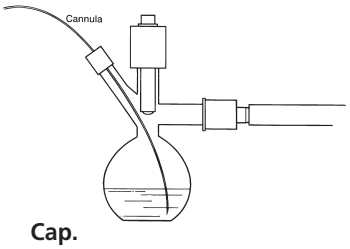
Designed for safe, reliable storage and dispensing of air-sensitive and odoriferous chemicals, pyrophorics, alkyllithiums, Grignards, corrosives, and purified or deuterated solvents.



Features:

- High-vacuum PTFE valve-to-glass seal eliminates air contamination in storage and septum leakage after initial needle penetration
- Heavy-wall, clear, borosilicate glass

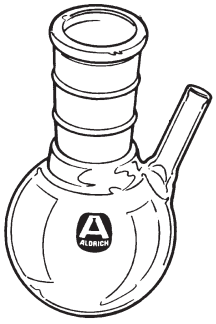




Cap. (mL)	Cat. No.	Cap. (mL)	Cat. No.
25	**Z40497-7**	500	**Z40501-9**
50	**Z40498-5**	1L	**Z40502-7**
100	**Z40499-3**	2L	**Z40503-5**
250	**Z40500-0**		

Flasks

Aldrich round-bottom flasks with septum-inlet



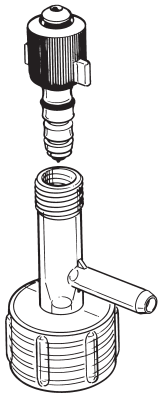
Cap. (mL)	⅀ Joint	Cat. No.
25	14/20	**Z10217-2**
50	14/20	**Z10218-0**
100	14/20	**Z10331-4**
250	14/20	**Z10332-2**
100	19/22	**Z10123-0**
250	19/22	**Z10124-9**
100	24/40	**Z10125-7**
250	24/40	**Z10126-5**
500	24/40	**Z10127-3**

Oxford Sure/Seal Storage Valve-cap

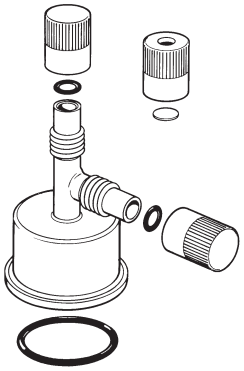
For use with Aldrich products packed in Sure/Seal bottles. Screws over Sure/Seal crown cap to permit repeated dispensing of product via syringe while ensuring positive valved closure. Technical Information Bulletin AL-195, with instructions in using the valve, is included.

Z40626-0

Replacement bottle-neck O-rings
Z42152-9



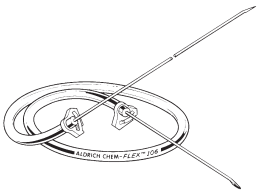
Aldrich Sure/Seal Septum-inlet Transfer Adapter



This inexpensive septum-inlet adapter screws over the Sure/Seal crown to permit repeated dispensing of product via syringe while protecting the contents of the bottle from air and moisture. The adapter allows for use of either an 8mm septum cap or standard rubber septa. 8mm septum cap (included) with flat PTFE-faced septum screws onto side arm for dispensing or short term storage. Standard rubber septa (**Z10072-2** or **Z12435-4**) fit on side arms for dispensing. For use with Aldrich products packed in Sure/Seal bottles.

Z40718-6

CHEM-FLEX™ Transfer Lines



These ready-to-use transfer lines incorporate CHEM-FLEX 106 tubing, which has a chemically-inert, thin-wall PTFE inner tube sheathed in clear PVC for extra strong, flexible lines that are resistant to crushing or kinking. Two 12- gauge SS needles (6 and 18in.) are connected to the CHEM-FLEX 106 tubing with nylon clamps. Liquids contact only PTFE and SS during transfers.

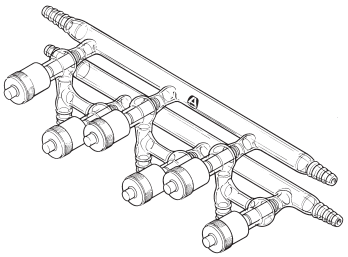
Tubing L (in.)	Cat. No.
30	**Z23102-9**
60	**Z28175-1**
120	**Z28177-8**

Natural Rubber Septa

For use with	*White rubber* Cat. No.	*Red rubber* Cat. No.
8 or 9mm o.d. glass tubing	**Z10072-2**	**Z12435-4**
9 or 10mm o.d. glass tubing	**Z10073-0**	**Z12436-2**
14/20 joints*	**Z10074-9**	**Z12437-0**
19/22 joints**	**Z10076-5**	**Z11830-3**
24/40 joints***	**Z10145-1**	**Z12439-7**

*Also fits Aldrich 2, 4, and 8oz narrow-mouth bottles.
**Also fits Aldrich 10, 32, 40oz, and 1L narrow-mouth bottles, and 125mL and 1L Sure/Seal bottles.
***Also fits Aldrich 64, 80oz, and 1gal narrow-mouth bottles.

Aldrich Vacuum Manifolds



Aldrich manifolds are available in a single or dual bank design for quick and easy access to vacuum or inert gas. A vacuum-gauge port is also offered as a means for relieving pressure build up. All versions accommodate ¼ in. i.d. tubing.

Glass stopcocks – 4mm bore

Positions	Overall L (mm)	*Single bank* Cat. No.	*Dual bank* Cat. No.
Standard manifold			
3	300	**Z53213-4**	**Z20268-1**
4	400	**Z53214-2**	**Z20270-3**
5	500	**Z53215-0**	**Z24357-4**
Manifold with vacuum-gauge port			
3	300	**Z53216-9**	**Z20267-3**
4	400	**Z53217-7**	**Z17443-2**
5	500	**Z53218-5**	**Z24356-6**

High-vacuum PTFE valves – 0-10mm J. Young valves

Positions	Overall L (mm)	*Single bank* Cat. No.	*Dual bank* Cat. No.
Standard manifold			
3	300	**Z53219-3**	**Z41413-1**
4	400	**Z53220-7**	**Z41415-8**
5	500	**Z53221-5**	**Z41416-6**
Manifold with vacuum-gauge port			
3	300	**Z53222-3**	**Z41562-6**
4	400	**Z53223-1**	**Z41563-4**
5	500	**Z53225-8**	**Z41564-2**

FORM: AL-134
0529-502662
0306