Transferring Air-Sensitive Reagents

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Background

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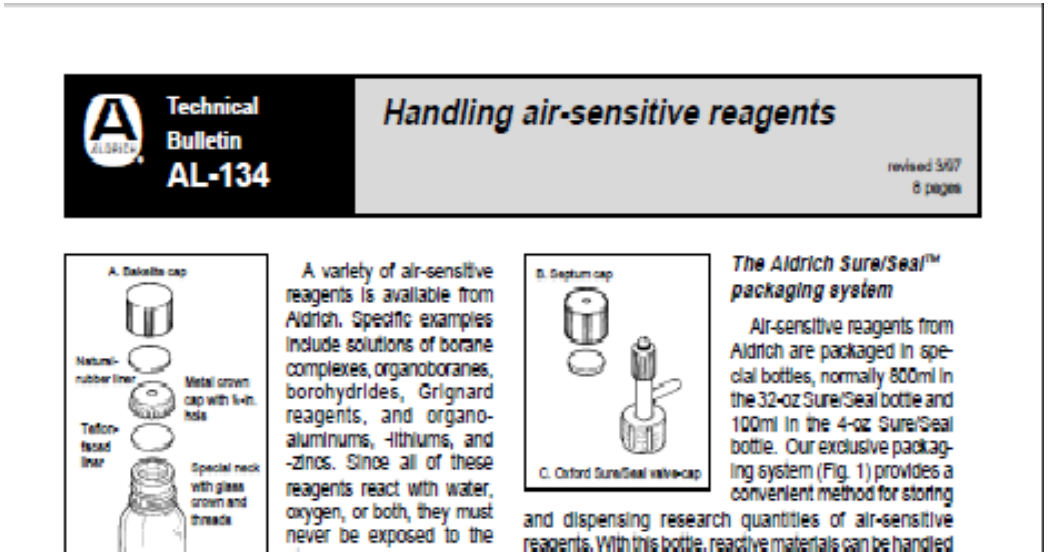
Introduction

- This presentation demonstrates recommended techniques for the transfer of air-sensitive reagents.
- Users of these materials should be technically trained & qualified lab workers.
- The information that will be presented in this talk is referenced from our Technical Bulletin AL-134 *Handling Air-Sensitive Reagents* and AL-164 *Handling Pyrophoric Reagents.*



Technical Bulletin
AL-134

Handling air-sensitive reagents

revised 3/07
8 pages

A. Bakelite cap
Natural-rubber liner
Metal crown cap with ¼-in. hole
Teflon-faced liner
Special neck with glass crown and threads

A variety of air-sensitive reagents is available from Aldrich. Specific examples include solutions of borane complexes, organoboranes, borohydrides, Grignard reagents, and organo-aluminums, -lithiums, and -zincs. Since all of these reagents react with water, oxygen, or both, they must never be exposed to the

B. Septum cap
C. Oxford Sure/Seal valve-cap

The Aldrich Sure/Seal™ packaging system

Air-sensitive reagents from Aldrich are packaged in special bottles, normally 800ml in the 32-oz Sure/Seal bottle and 100ml in the 4-oz Sure/Seal bottle. Our exclusive packaging system (Fig. 1) provides a convenient method for storing and dispensing research quantities of air-sensitive reagents. With this bottle, reactive materials can be handled

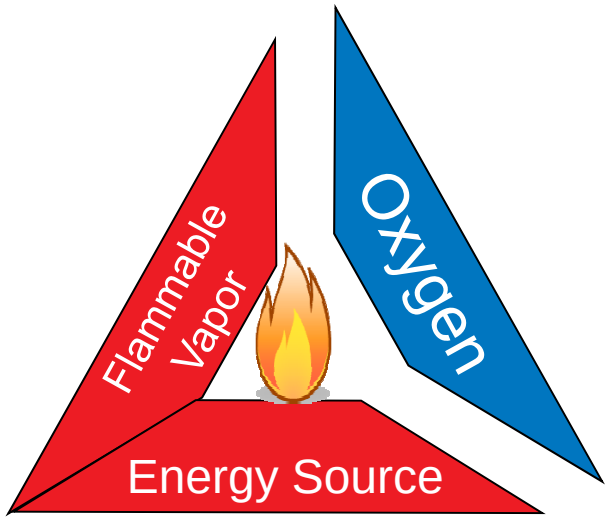
Aldrich Technical Bulletins may be accessed at sigma-aldrich.com/techbulletins

Video→

What Makes These Reagents Dangerous?

Air-Sensitive reagents can:

- be pyrophoric – ignite spontaneously in air
- react violently with water
- liberate extremely flammable gases when in contact with water



Pyrophoric Substance

Video→

Identifying Air-Sensitive Reagents as Pyrophoric

Alkyl metals (*e.g.* trimethylaluminum, diethylzinc, t-butyllithium, etc.)

- Compounds with M—CR_3 bonds, M = any metal or transition metal atom
- Alkyl group corresponds to a flammable gas or vapor as H—CR_3

Hydrides (*e.g.* sodium hydride, borane, phosphine etc.)

- Compounds with M—H bonds, M = anything except C, N, O, S, Se, or halogen

Highly active metals (*e.g.* sodium, catalysts, activated metals)

The Material Safety Data Sheet

The label on the bottle

SIGMA-ALDRICH

FW 98.00; bp 95 °C/760 mmHg; mp -93 °C; d 0.677;
US Pyrophoric Toxic. EU Extremely Flammable. Corrosive.
Spontaneously flammable in air. May form explosive peroxides. Harmful if swallowed. Causes burns. Vapors may cause drowsiness and dizziness. Keep container tightly closed. Keep away from sources of ignition - no smoking. Take precautionary measures against static discharges. Do not breathe vapor. In case of contact with eyes, rinse immediately with plenty of water and seek medical advice. Wear suitable protective clothing, gloves, and eye/face protection. In case of fire, use dry powder. Never use water. In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible). Toxic if inhaled. Toxic if ingested. Target organ(s): Central nervous system. Kidneys. Handle and store under inert gas. Air sensitive. Light sensitive. Heat sensitive.

Product of USA. MSDS available. SF09211. For R&D use only. Not for drug, household or other uses.

Caution: Substance not yet fully tested.

594377-100ML Batch #:16320BB

Triethylborane, 2.0*M* solution in ether

Technical bulletin AL-134(Handling Air-Sensitive Reagents) available at sigma-aldrich.com.

Extremely Flammable. Corrosive.

The Material Safety Data Sheet

- sigmaaldrich.com

Prepare Yourself

Understand the hazards of the chemicals that will be used

- Read labels
- Read MSDS sheets
- Concentration or composition

Choose less-reactive reagents where possible

- *n*-butyllithium versus *t*-butyllithium
- Lower concentrations versus higher concentrations

Prepare the work area

- Remove combustible materials and flammable solvents from the area
- Perform transfer in a fume hood with a drop sash
- Also use a safety shield if you are working with large-scale equipment
- Make sure a qualified co-worker is present and is aware of what you are doing
- Remove any obstructions from your escape routes

Prepare Yourself (continued)

Use proper personal protective equipment

- Goggles
- Fire-resistant lab coat
- Nitrile gloves
- Additional face shield when transferring large liquid volumes

Identify the locations of safety equipment

- Safety shower/eye wash station
- Appropriate fire extinguishers and suppressant materials

Prepare for the worst—be ready for a fire

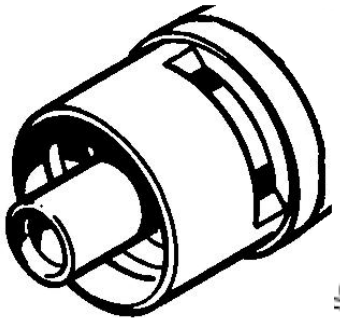
- Do not wear flammable synthetic clothing
- Know your escape route

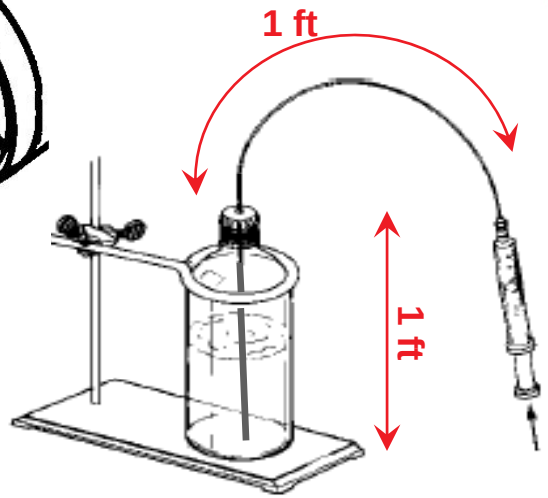
Plan your procedure thoroughly and execute it confidently

Setup—Syringes

Choose proper equipment

- Needle-lock Luer syringes prevent separation of needle and syringe
- Long flexible needles (1-2 feet) permit inversion of the syringe during filling and transfer
- Small-gauge needles (no larger than 16 gauge) resist unwanted dripping and better preserve the seal on the reagent bottle septum
- Select a syringe with a capacity of twice the total volume to transfer
- Absolute maximum 100mL syringe (large syringes are clumsy to use)
- Avoid using a syringe for multiple draws in the same transfer (use a larger syringe or a double-tipped needle instead)





Setup - Equipment (continued)

Check to see if the equipment works

- Check the needle for blockages by passing nitrogen through it and placing the needle's other end in a liquid to look for bubbles.
- Check glassware for defects and cracks. When in doubt do not use.
- Check the syringe for leaks.
- Check the addition funnel for leaks.

Video→

Setup – Equipment (continued)

Oven dry all glassware

Flush inert gas through all vessels and transfer lines

- Use a bubbler line to flush the syringe.
- Use a regulated (3 to 5 psi) pressure line to flush out vessels.

Secure all vessels you will be using with clamps so that you have both hands free for other operations.

Assemble a bubbler for venting the reagent vessel.

Procedure

Transfer of the air-sensitive reagent can be accomplished by one of two methods.

- Syringe (glass recommended)
- Double-tipped needle

For transferring small volumes (50mL or less) at one time, you can use a syringe.

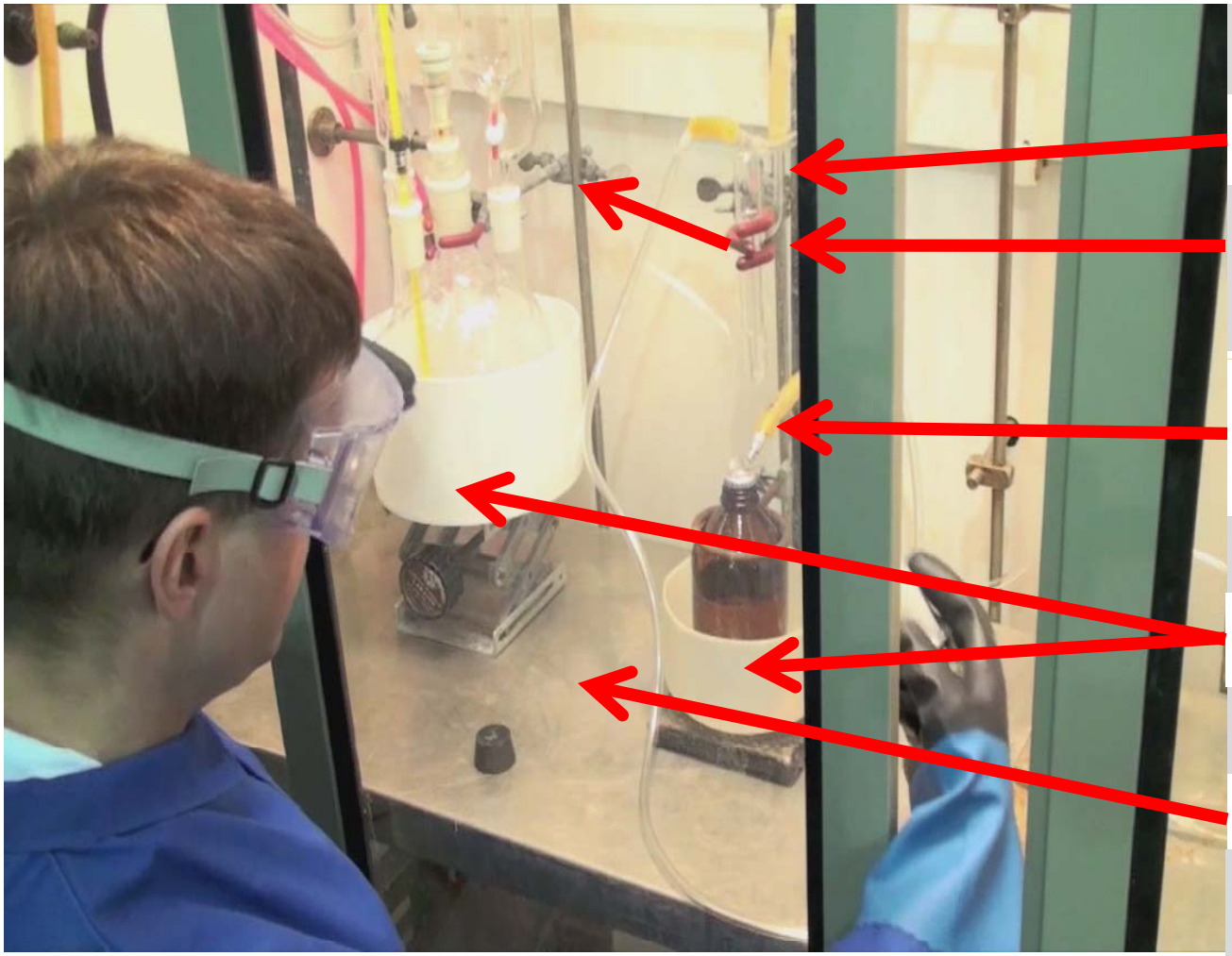
For larger volumes (50mL or more) use a double-tipped needle.

The procedure using a glass syringe will be slightly different compared to a plastic syringe

- With a glass syringe you will use an inert gas-pressurized reagent vessel to transfer the reagent to the syringe.
- With a plastic syringe you will use a reagent vessel on a bubbler and pull the plunger up to draw the reagent into the syringe.

Video→

Syringe Safety Illustrated



hood doors drawn

vent line bubbler

bottle and reaction vessel clamped

3-5psi inert gas on bottle

full eye protection

containment

nitrile gloves

clutter removed

flame-retardant lab coat

Syringe Method Recap

50-mL transfer maximum (no more than half of syringe capacity)

Use only needle-lock Luer syringe.

Check syringe needle for plugs.

Check addition funnel for leaks around stopcock.

Use 3-5 psi inert gas on reagent bottle to push liquid into glass syringe (lower or neutral pressure if plastic).

Slightly overfill syringe, then vent pressure on bottle, and push vapor pocket and excess back into reagent bottle.

Push vapor pocket into vented addition funnel first, then push liquid into addition funnel, leaving pocket of liquid in syringe tip.

Destroy pocket of liquid remaining in syringe as part of clean up.

Double-Tipped Needle Safety Illustrated

- clutter removed
- nitrile gloves
- full eye protection
- face shield (Added)
- flame-retardant lab coat
- bottle and reaction vessel clamped
- containment
- vent line bubbler
- 3-5psi inert gas on bottle

Double-Tipped Needle Method Recap

Any volume over 10mL

Check double-tipped needle for plugs.

Check addition funnel for leaks around stopcock.

Use 3-5 psi inert gas on reagent bottle to push liquid into addition funnel on vented apparatus.

Do not overfill addition funnel; meter last few mL of transfer by lifting needle to surface of liquid in bottle.

Blow needle dry with inert gas (3-5 psi) at conclusion of liquid transfer.

Clean needle immediately after transfer.

Cleanup

When the proper amount of liquid is delivered to the reaction vessel, a small amount of material will remain in the needle and syringe

Rinse out the liquid in the syringe by placing the needle in an inert (non-reacting) solvent and pumping (at least 3 times) the syringe plunger

Rinse out the remaining liquid in the syringe by placing the needle in alcohol and pumping the syringe plunger

The syringe and needle can then be cleaned as normal with water

The wash solvent can be safely combined with other waste solvents

The double-tipped needle that was blown dry can be cleaned as normal with water

Conclusion

Do's

- Do understand all of the hazards involved with any material you use.
- Do work in a chemical fume hood.
- Do wear proper personal protective equipment.
- Do plan your work with dangerous materials thoroughly in advance.

Don'ts

- Don't use untested equipment.
- Don't use a syringe to transfer a volume greater than 50 mL.
- Don't work with dangerous materials alone.
- Don't panic in the event of a fire.