



SAFE OPERATING PROCEDURE PYROPHORIC REAGENTS ORGANOLITHIUM REAGENTS

Definition

Pyrophoric materials are those that ignite spontaneously in air below 45°C (130°F). They react with water in the air, oxygen, or both. Pyrophorics can be solid, liquid, or gaseous. Solids and liquids are often stored under kerosene or an inert gas. The pyrophoric hazard increases as the pyrophoric's concentration increases. Examples of pyrophorics include Grignard reagents, metal alkyls and aryls, metal carbonyls, metal powders, metal and nonmetal hydrides, nonmetal alkyls, white phosphorous, silane, phosphine, arsine, borane, diborane, and alkylsilanes. These reagents must be handled to rigorously exclude air and moisture.

Hazards

Even for experienced handlers, pyrophorics present risks. The most likely source of moderate to severe injury from direct contact with a pyrophoric is from fire. If the material ignites, a secondary fire can result and damage the surrounding lab areas and beyond. Other common hazards include corrosivity, teratogenicity, water reactivity, and peroxide formation, along with damage to the liver, kidneys, and central nervous system.

Handling

TRAINING. All users must be specially trained by their PI/faculty member or experienced user of pyrophorics. Read and understand the MSDS and this SOP before you use the pyrophoric material.

STORAGE. Always store pyrophorics under an inert gas or kerosene. A glove box under N₂ is the best place for them. If you don't have a glove box, a controlled atmosphere bag is acceptable.

- Keep the original shipping container with absorbent and use both to protect the bottle from shocks and spills.
- Do not store pyrophorics with ordinary flammables in a flammable cabinet.
- Do not store pyrophorics near sources of ignition.
- Minimize quantity of pyrophorics necessary in the lab.

OPERATIONS. Assess the risks before you start work with pyrophorics. Detail experiments in advance, especially the technique(s) for material transfers. Several sources are listed in the Reference section of this SOP.

- **NEVER work alone when using pyrophorics.**
- **Use pyrophorics during normal working hours, such as 8-6 M-F.**
- Remove all nonessential reagents and equipment from the area where you use pyrophorics.
- Never allow combustible materials to contact pyrophorics at any time.



- Never return unused pyrophorics to the original container. Small amounts of impurities may be introduced into the container, which may cause a fire or explosion.
- Many pyrophoric chemicals release noxious or flammable gases, so handle pyrophorics in a fume hood with a spill tray. Keep the sash at the lowest possible height.
- Conduct operations in a manner to prevent the pyrophoric's exposure to the atmosphere. Several techniques, depending on the physical state and quantity of pyrophorics used, are available to you. These techniques range from use of gas-tight syringes to glove boxes.
- Transfer pyrophorics by syringe fitted with a lockable needle to prevent the needle from being dislodged accidentally. For the transfer of large amounts use a cannula pressurized by an inert gas. However, carefully avoid over-pressuring containers.
- Use small syringes. If handling more than 20 mL of sample, use a cannula for transfer or use a 20 mL syringe repeatedly.
- Keep dry sand nearby as a fire extinguishing medium. A small beaker or two of sand is useful to extinguish any fire that occurs at the syringe tip and to receive any last drops of reagent from the syringe.
- Evacuated glassware can implode and eject flying glass and splattered chemicals. Conduct vacuum work involving pyrophorics in a fume hood or glove box.
- Vacuum pumps should be rated for use with pyrophoric chemicals.
- Protect mechanical vacuum pumps by using cold traps and, where appropriate, filters to prevent particulate release. Vent the exhaust from the pumps into an exhaust hood.

Personal Protective Equipment (PPE)

1. Wear chemical splash goggles or safety glasses that meet the Practice for Occupational and Educational Eye and Face Protection (ANSI Z.87.1 1989) standard. If the potential for splashing or a highly exothermic reaction exists, wear a face shield over your safety glasses. Ordinary prescription eyeglasses will **not** provide you with sufficient eye protection.
2. In addition, you should use a portable device such as a Unishield to protect your face and body. Safety shielding is required any time a risk of explosion, splashing, or a highly exothermic reaction is present. If you don't have a portable shield, you must use pyrophoric chemicals in a fume hood with the sash in the lowest feasible position.
3. Long Cuff gloves with thin mil nitrile under them are the appropriate hand protection. If these are unavailable, wear nitrile gloves underneath neoprene gloves.
4. Do not wear a lab coat or apron made from an easily-ignited material like nylon or polyester. Instead wear a fire-resistant lab coat such as Nomex. Your clothes should be cotton or wool instead of synthetic materials, which when burned melt and adhere to your skin.
5. Of course, you should always wear long sleeves, long pants, and completely-closed shoes.



Disposal

1. Do not leave a container with any residue of pyrophoric materials open to the atmosphere.
2. To destroy pyrophorics, transfer any unused or unwanted materials to an appropriate reaction flask for hydrolysis and/or neutralization with adequate cooling.
3. Rinse the essentially empty container three times with an inert dry solvent; then neutralize or hydrolyze this rinse solvent.
4. After you triple-rinse the container, leave it open in back of a hood or glove box at a safe location for at least a week. After the week, triple-rinse the container again.
5. Dispose of all materials contaminated with pyrophorics as hazardous waste.
6. Do not mix neutralized pyrophorics with other hazardous waste, especially flammables. Keep them in a separate container.
7. Do not leave pyrophoric waste open overnight in the laboratory. It must be properly contained to prevent fires.
8. Call EH&S (817-272-2185) and request pickup of the waste materials that day. **Specify that you have pyrophoric waste** and that you need same-day pickup.

Small Spills

Anticipate small spills by having the appropriate cleanup equipment readily available, such as sand. The appropriate cleanup supplies can be determined by consulting the MSDS. You should do this prior to using any pyrophoric chemical. Spill control materials for oxidizers are designed to be inert and will not react with the reagent.

Emergency Procedures

As described above, use dry sand or powdered lime to completely smother and cover any small spill that occurs.

Do not attempt to handle a large spill of pyrophoric materials yourself. Turn off all ignition sources and vacate the laboratory immediately. Call UTA Police Dispatch for assistance, 817-272-3003. Remain on the scene, but at a safe distance, to receive and provide information to safety personnel when they arrive.

The recommended fire extinguisher is a standard dry powder (ABC) type. Class D extinguishers are recommended for combustible solid metal fires (e.g., Na, LAH), but not for organolithium reagents. Do not use carbon dioxide or water fire extinguishers as these types of extinguishers can actually enhance the combustion of some pyrophoric compounds.

If you are exposed to pyrophoric materials, or on fire, wash yourself with copious amounts of water in the safety shower and seek medical attention immediately.



References/For More Information

Extensive list of pyrophoric compounds <http://www.doctorfire.com/Pyrophoric.html>

Extensive guides to handling pyrophorics

http://www.sigmaaldrich.com/etc/medialib/docs/Aldrich/Bulletin/al_techbull_al134.Par.0001.File.tmp/al_techbull_al134.pdf

http://www.sigmaaldrich.com/etc/medialib/docs/Aldrich/Bulletin/al_techbull_al164.Par.0001.File.tmp/al_techbull_al164.pdf

http://www.sigmaaldrich.com/etc/medialib/docs/Aldrich/Bulletin/al_techbull_al166.Par.0001.File.tmp/al_techbull_al166.pdf

http://membership.acs.org/c/chas/techarchive/organolithium_in_labs.pdf

Transfer techniques diagrammed

<http://www.ehs.ucr.edu/resources/SOPs/Procedures%20for%20Safe%20Use%20of%20Pyrophoric%20Organolithium%20Reagents.pdf>

Miscellaneous information

<http://ehs.unl.edu/sop/s-pyrophoric.pdf>

http://cameochemicals.noaa.gov/reactivity#Pair_1

<http://safetyservices.ucdavis.edu/environmental-health-safety/safetynets/master-list-1/safety-net-135>

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