UCI Environmental Health & Safety

Standard Operating Procedure (SOP)

This Standard Operating Procedure (SOP) describes basic chemical safety information for pyrophoric chemicals. Prior to conducting work with pyrophorics personnel must obtain approval from their Principal Investigator (PI) and/or Supervisor and attend the appropriate laboratory safety training. The PI must complete the Lab-Specific Use Procedures section and provide their personnel with a copy of this SOP and a copy of the SDS from the manufacturer.

Pyrophoric Chemicals

Date SOP was written:	
Date SOP was approved by PI/lab supervisor:	
Principal Investigator:	
Principal Investigator Signature:	

Type of SOP: ☐ Process ☐ Hazardous Chemical [X] Hazardous Class

Purpose

The purpose of this standard operating procedure is to acquaint you with the proper and safe handling, use, storage, and disposal of pyrophoric chemicals.

Properties & Hazards

Definition from the National Fire Protection Agency (NFPA):

Pyrophoric chemicals are defined as chemicals that spontaneously ignite in air at or below a temperature of 130 °F (54.5 °C) or chemicals with an autoignition temperature in air at or below 54.4 °C (130 °F).

GHS Pictogram	UCI Hazard Level	GHS Category	GHS H-Code	Cal/OSHA Definitions
	Highly Hazardous	Pyrophoric Liquids/Solids (Cat. 1)	H250	(none)

All chemicals in this band are considered highly hazardous.

General Hazards:

Pyrophoric materials ignite spontaneously on contact with atmospheric oxygen, moisture in the air, or both. Therefore, pyrophoric materials should only be handled under an inert atmosphere. Failure to follow proper handling procedures can result in fire or explosion, leading to serious injuries or death, and significant damage to facilities. Some examples of pyrophoric chemicals include grignard reagents (e.g. RMgX), metal alkyls and aryls (e.g. tert-butyllithium, n-butyllithium, phenyllithium), metal carbonyls (e.g. lithium carbonyl, nickel tetracarbonyl), finely divided metal powders (e.g. cobalt, iron, zinc, zirconium, lithium), and non-metal alkyls (e.g. R_3B, R_3P, R_3As).

Additional Hazards:

Many pyrophorics are sold/used as solutions in flammable solvents, which may exacerbate any dangerous reactions that can occur with misuse of these reagents. In addition, pyrophoric chemicals tend to exhibit additional hazards such as target organ toxicity, reproductive toxicity, corrosivity, water reactivity, and peroxide formation.

Personal Protective Equipment (PPE)

Skin and Body Protection:
A flame resistant Nomex® lab coat, long pants (or equivalent) completely covering legs, and closed toed shoes must be worn. Never wear synthetic clothing when working with pyrophorics.

Hand Protection:
If handling outside of a glovebox, fire-resistant hand protection is required, including a chemical resistant outer glove (neoprene) over an approved fire-resistant (Nomex®) inner glove/liner.

Eye Protection:
ANSI Z87.1-compliant safety glasses or safety goggles if a splash hazard is present. If an explosion or high fire hazard is present, a face shield over safety glasses is recommended.

Administrative Controls

- Never work alone with pyrophoric chemicals. Inform all other personnel in the laboratory before working with these chemicals.
- Review the Safety Data Sheets (SDSs) for all chemicals used in the experiment. Online SDSs can be accessed at https://www.ehs.uci.edu/sds/index.php.
- Conduct a 'dry run' with low hazard materials.
- Researchers must be trained and demonstrate a proficiency in handling pyrophoric materials prior to work.

Engineering Controls

Gloveboxes:
Gloveboxes provide an inert and dry atmosphere making them the recommended engineering control to use when working with pyrophoric chemicals.

Fume Hoods:
An inert atmosphere (nitrogen or argon) manifold Schlenk line is a good alternative when working with pyrophoric chemicals, if a glovebox is not available or cannot be used. Proper manipulation of Schlenk manifolds will avoid exposure of these reagents to air and water.

Gas Cabinets:
Storage of pyrophoric gases is described in the California Fire Code, Chapter 64. Gas cabinets storing pyrophoric gases are required to have the appropriate remote sensors and fire suppression equipment. Gas flow, purge, and exhaust systems should have redundant controls to prevent pyrophoric gas from igniting or exploding. All pyrophoric gases must have Restricted Flow Orifices (RFO) installed on the cylinder. Emergency back-up power should be provided for all electrical controls, alarms, and safeguards associated with the pyrophoric gas storage and process systems.

Special Storage and Handling Requirements

Storage:
- Pyrophoric reagents can only be handled and stored in fully-sprinklered buildings.
- Pyrophoric reagents must be handled and stored under an inert atmosphere in a manner to avoid exposure to atmospheric oxygen and moisture.

- Containers of pyrophoric materials and storage locations must be clearly labeled.
- Pyrophoric chemicals must be stored away from incompatible materials including combustible materials, oxidizing acids, oxidizers, and aqueous solutions.
- Store pyrophoric chemicals in a flammable storage cabinet, refrigerator/freezer rated for flammable storage, glovebox, or a desiccator. Consult the SDS for the most appropriate storage location and ensure proper segregation.
- If pyrophoric reagents are received in a specially designed shipping, storage, or dispensing container, ensure that the integrity of that container is maintained.
- Ensure that sufficient protective solvent, oil, kerosene, or inert gas remains in the container while the material is stored.

Handling:

- NEVER work alone. At least one other person must be informed and present in the same room while work with pyrophoric chemicals is being conducted.
- When possible, run reactions with pyrophoric reagents in an inert atmosphere glovebox.
- Pyrophoric solids must be transferred under an inert atmosphere in a glovebox. Pyrophoric liquids may be transferred within a glovebox or using proper syringe, cannula, or Schleck techniques. Cannulation should be used when transferring any amounts greater than 20 mL.
- Pyrophoric gases should be handled in compliance with California Fire Code, Chapter 64.
- Ensure that the work area is adequately prepared prior to the experiment (e.g. remove all combustible materials [including paper towels and Kimwipes], remove all excess or nonessential chemicals and equipment from the area).
- A container of powdered lime, dry sand, and/or liquid nitrogen should be kept within arm's length when working with pyrophoric materials (these can be used to smother a small spill).
- NEVER return excess chemical to the original container (small amounts of impurities introduced into the container may cause a fire or explosion).

Spill, Accident, and First Aid Procedures

Spills:

If pyrophoric chemicals spill within a glovebox, quench the materials, absorb the spill with non-combustible materials, and dispose of the materials as hazardous solid waste. Powdered lime or dry sand can be used to cover and contain a small spill outside of a glovebox. Notify your supervisor and EHS at x4-6200 immediately.

Skin or Eye Contact:

Remove contaminated clothing or contact lenses and flush the affected area with water for at least 15 minutes. Obtain medical attention immediately.

Inhalation:

Move to fresh air. Obtain medical attention immediately.

Ingestion:

Obtain medical attention immediately. (The poison control center, (800) 222-1222, is available 24 hours every day).

Fire:

Pull the fire alarm and evacuate the area. NEVER use a water or a carbon dioxide fire extinguisher, these can enhance combustion. A Class D fire extinguisher is recommended for

combustible solid metal fires (e.g. sodium), and a standard dry powder (ABC) fire extinguisher is recommended for other materials.

Waste Disposal Procedure

Quenching:

- Used pyrophoric materials should be quenched under an inert atmosphere with adequate cooling. Do not return pyrophoric materials to their original container.
    - Never quench pyrophoric materials with water.
    - Refer to a published quenching procedure.
    - If a published quenching procedure is not available, the following procedure can be used to quench the majority of pyrophoric and water reactive materials: slowly add isopropanol under an inert atmosphere while cooling and stirring.

Disposal:

- NEVER leave a container or waste bottle with residue or pyrophoric materials open to the atmosphere. These materials should always be contained to prevent fires.
- Hazardous waste must be transferred to EHS for disposal within 6 months of being generated.
- Hazardous Waste Disposal
    - Text to pick up to hwp@uci.edu, EHS will pick up your waste within 1-3 days
    - Or visit https://ehs.uci.edu/enviro/haz-waste/

Additional Information

For additional information about handling explosives and potentially explosives refer to:;

- UCI Chemical Hygiene Plan: https://www.ehs.uci.edu/programs/_pdf/lab-res/chemical-hygiene-plan.pdf
- Pyrophoric safety video: https://www.youtube.com/watch?v=21iC4YEgOAs
- Prudent Practices in the Laboratory: Handling and Management of Chemical Hazards (section 4.D.2.2 “Pyrophorics” The National Academies Press: Washington, DC, 2011. (https://nap.nationalacademies.org/catalog/12654/prudent-practices-in-the-laboratory-handling-and-management-of-chemical).
- Aldrich Technical Information Bulletin AL-134: https://www.sigmaaldrich.com/deepweb/assets/sigmaaldrich/marketing/global/documents/685/583/al_techbull_al134.pdf?srsltid=AfmBOoqrr3dnvUZ2ByPg17GKkq5WomYgekV4_Og20JJsrfMB_5qwNSF
- Aldrich Technical Information Bulletin AL-164: https://www.sigmaaldrich.com/content/dam/sigma-aldrich/docs/Aldrich/Bulletin/al_techbull_al164.pdf
- Aldrich Technical Information Bulletin AL-195: https://www.sigmaaldrich.com/content/dam/sigma-aldrich/docs/Aldrich/Bulletin/al_techbull__al195.pdf.
- Pyrophoric gases should be handled in compliance with the California Fire Code, Chapter 64: https://www.citymb.info/Home/ShowDocument?id=28089.

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APPENDIX A:
Lab-Specific Use Procedures

The following procedures describe how the subject chemicals are used in this laboratory beyond the practices described above.

Please see the General Information for ***Hazardous Materials Standard Operating Procedure*** for specific instructions on writing lab-specific use produces.

This section must describe lab-specific procedures to address the safe use of all highly hazardous chemicals from this band in use in the laboratory. These procedures may be organized around specific chemicals, specific tasks or the band as a whole.

Documentation of Training

Prior to conducting any work with pyrophoric chemicals, designated personnel must provide training to their laboratory personnel specific to the hazards and procedures involved in working with these substances.

I have read and understand the content of this SOP:

Name	Signature	Date