

Pyrophoric Materials

STANDARD OPERATING PROCEDURE (SOP)

Type of SOP: Process Hazardous Chemical Hazardous Class

All personnel subject to these SOP requirements must review a completed SOP and sign the associated training record. Completed SOPs must be kept with the UC Davis Laboratory Safety Manual or be otherwise readily accessible to laboratory personnel. Electronic access is acceptable. SOPs must be reviewed, and revised where needed, as described in the [UC Davis Laboratory Safety Manual](#). Note that not all hazardous chemicals are appropriately addressed in a single control-banded SOP, and some chemicals are subject to several control-banded SOPs. Unique properties of each chemical must be considered before including it into a control band.

Date SOP Written:	Click here to enter a date. _____	Approval Date:	Click here to enter a date. _____
SOP Prepared by:	<u>REQUIRED - Insert Preparer's Name</u> CLSC SOP Task Force		
SOP Reviewed and Approved by (name/signature):	<u>REQUIRED - Insert Approver's Name & Signature</u>		
Department:	<u>REQUIRED - Insert Department</u>		
Principal Investigator/ Laboratory Supervisor:	<u>REQUIRED - Insert Name</u>	Phone:	<u>REQUIRED - Insert Phone#</u>
Lab Manager/ Safety Coordinator:	<u>REQUIRED - Insert Name</u>	Phone:	<u>REQUIRED - Insert Phone#</u>
Emergency Contact(s):	<u>REQUIRED - Insert Name</u>	Phone:	<u>REQUIRED - Insert Phone#</u>
	_____		_____
	_____		_____
	_____		_____
Location(s) covered by SOP:	Building: <u>REQUIRED - Insert Name</u>	Lab	
	Room #(s): <u>REQUIRED - Insert Number</u>	Phone:	<u>REQUIRED - Insert Phone#</u>

1. HAZARD OVERVIEW

Pyrophoric materials are substances that can ignite spontaneously upon exposure to air or oxygen. They can also be water-reactive, where heat and a flammable gas are produced. For Pyrophoric materials, oxidation of the compound by oxygen or moisture in air proceeds so rapidly that ignition occurs.

2. HAZARDOUS CHEMICAL(S)/CLASS OF HAZARDOUS CHEMICAL(S)

Typical Pyrophorics include, but are not limited to: metal hydrides, select finely divided metal powders, nonmetal hydride and alkyl compounds, white phosphorus, alloys of reactive materials, Grignard reagents, and some organometallic compounds (including alkyllithium, and alkylzinc reagents).

Materials that may spontaneously auto-ignite can be identified using the Globally Harmonized System using the Hazard Codes of H-250 (Catches fire spontaneously if exposed to air) and H-260 (In contact with water releases flammable gases which may ignite spontaneously).

REQUIRED - List (or attach) the applicable chemical(s) for your laboratory, and describe important properties and signs/symptoms of exposure.

3. ENGINEERING/VENTILATION CONTROLS

The following is a general plan for all Pyrophorics:

- Work under an inert and dry atmosphere (argon, nitrogen) in an enclosed glove box.

If work in a glove box is impractical or otherwise not possible:

- Work inside a properly functioning certified chemical fume hood using air-free (e.g., Schlenk) technique when handling Pyrophoric materials. Work with the sash as low as possible;
- Work away from water sources or potential water splash;
- Remove adjacent ignition sources and unneeded flammable/combustible materials;
- Use fresh dry solvents; and
- If materials or side products are prone to rapid decomposition, use a portable blast shield.

REQUIRED - Insert descriptions of the lab-specific ventilation controls and equipment safety features utilized to reduce the risk of Pyrophoric chemical exposures.

4. ADMINISTRATIVE CONTROLS

The following elements are required:

1. Complete the [UC Laboratory Safety Fundamentals](#) (or approved equivalent) training prior to working in the laboratory;
2. Complete laboratory-specific safety orientation and training on laboratory-specific safety equipment, procedures, and techniques to be used, including any applicable laboratory-specific Laboratory Safety Plan(s), prior to receiving unescorted access to the laboratory;
3. Demonstrate competency to perform the procedures to the Principal Investigator (PI), Laboratory Supervisor, laboratory-specific Safety Officer, and/or trainer;
4. Be familiar with the location and content of any applicable Safety Data Sheets (SDSs) for the chemicals to be used (online SDSs can be accessed from [UC SDS](#));
5. Implement good laboratory practices, including good workspace hygiene;
6. Inspect all equipment and experimental setups prior to use;
7. Follow best practices for the movement, handling, and storage of hazardous chemicals (see Chapters 5 and 6 of [Prudent Practices in the Laboratory](#) for more detail). An appropriate spill cleanup kit must be located in the laboratory. Chemical and hazardous waste storage must follow an appropriate segregation scheme and include appropriate labeling. Hazardous chemical waste must be properly labelled, stored in closed containers, in secondary containment, and in a designated location;

8. Do not deviate from the instructions described in this SOP without prior discussion and approval from the PI and/or Laboratory Supervisor; and
9. Notify the PI and/or Laboratory Supervisor of any accidents, incidents, near-misses, or upset condition (e.g., unexpected rise or drop in temperature, color or phase change, evolution of gas) involving Pyrophorics described in this SOP.

For Pyrophorics, the following are also required:

10. Never work alone. All work involving Pyrophorics must be performed in the presence of at least one safety buddy. The safety buddy must be a person who has been trained in the use of Pyrophorics and who is proficient with the Pyrophoric emergency protocols set forth in this SOP. Furthermore, the safety buddy must be within audible and visible range of the person that is handling Pyrophorics at all times, and must not be concurrently working with Pyrophorics or any other compound or process that cannot be easily and safely abandoned;
11. Any individual using Pyrophorics must be trained on all information contained within [SafetyNet #135](#);
12. It is better to do multiple transfers of small volumes (less than 10 mL) than attempt to handle larger quantities. Never transfer more than one aliquot using same syringe. Never transfer more than half of the volume contained by a syringe (e.g., do not transfer more than 5mL of liquid in a 10 mL syringe). Liquids may be safely transferred without a glove box by employing certain syringe or cannula techniques. For large volume transfers the cannula technique should be considered. Before transferring, make sure that the material is at the appropriate temperature [see SDS]. See [SafetyNet #135](#) for further details;
13. Ensure all equipment is dry, damage-free, air-free, clean, and appropriate for the task;
14. Be sure to have a quenching scheme for residual materials prior to beginning work;
15. Clear the area of unrelated and incompatible hazards;
16. Know the location of eye wash/safety shower and first aid kit. Only use if the area is properly equipped with this safety equipment located within ten seconds of travel;
17. You **must** have an appropriate extinguishing agent (dry sand, Met-L-X, soda ash, or lime) for the Pyrophoric material you are using immediately available adjacent to your workspace. Extinguishing agents for Pyrophorics are not provided by campus Fire Prevention and must be obtained by the lab personnel working with Pyrophorics;
18. Pyrophorics shall have their own dedicated storage with secondary containment and segregated from incompatibilities. Pyrophoric gases shall be stored in compliance with California Fire Code requirements. Please contact the Chemical Hygiene Officer for storage recommendations and requirements
19. Minimize your purchases of Pyrophoric materials to quantities that will be used within one year. The date of receipt and date of opening must be written onto the container. Contact the Chemical Hygiene Officer for the storage restrictions for your specific laboratory/building.

REQUIRED - Insert the laboratory-specific restrictions on maximum quantities to be used and stored. Include lab-specific transfer procedure(s), volume threshold for syringe/double cannula transfer methods, and any equipment restrictions.

Storage Considerations for Pyrophorics:

- When appropriate store under inert (e.g., N₂, Ar) gas;
- Store all pyrophoric materials in the manufacturer's container;

- Avoid heat/ flames, ignition sources, oxidizers, protonating substances (e.g., acids, alcohols, etc.), and water sources; and
- It should be noted that the storage requirements of the individual materials must be considered (e.g. alkyllithium species should not be stored near strong Lewis acids despite the similar storage requirements for the two species).

REQUIRED - Insert descriptions of lab-specific storage, segregation, and any special handling requirements for each chemical or group of chemicals.

5. PERSONAL PROTECTIVE EQUIPMENT (PPE)

At a minimum, long pants (covered legs) and closed toe/closed heel shoes (covered feet) are required to enter a laboratory or technical area where hazardous chemicals are used or stored.

In addition to the minimum attire required upon entering a laboratory, the following PPE is required for all work with Pyrophorics:

- A. Eye Protection:
 - i. At a minimum ANSI Z87.1-compliant safety glasses are necessary.
 - ii. Splash goggles may be substituted for safety glasses, and are required for processes where splashes are foreseeable or when generating aerosols.
 - iii. Ordinary prescription glasses will NOT provide adequate protection unless they also meet the Z87.1 standard and have compliant side shields.
- B. Body Protection: At a minimum a flame-resistant (FR) laboratory coat that is NFPA 2112-compliant laboratory coat that fully extends to the wrist is necessary.
 - i. Clothing worn under PPE should not be made from synthetic materials;
 - ii. For chemicals that are corrosive and/or toxic by skin contact/absorption additional protective clothing (e.g., face shield, chemically-resistant apron, disposable sleeves, etc.) are required where splashes or skin contact is foreseeable.
 - iii. When using/transferring/quenching Pyrophorics in a chemical fume hood a face shield should be considered any time there is a need to raise the sash above the standard 18-inch opening height for any extended period of time.
- C. Hand Protection: Hand protection is needed for the activities described in this SOP. Define the type of glove to be used based on: A) the chemical(s) being used, B) the anticipated chemical contact (e.g., incidental, immersion, etc.), C) the manufacturers' permeation/compatibility data, and D) whether a combination of different gloves is needed for any specific procedural step or task.

When handling Pyrophorics:

- a. A chemically-compatible glove of at least 10-mil thickness, or double-gloving of gloves at least 5-mil thickness, shall be used;
- b. Flame-resistant (e.g., Nomex) gloves may be used in conjunction with a chemically-compatible disposable glove, and should be considered when an elevated risk of Pyrophoric spill exists (e.g., movement of Pyrophorics)

See [SafetyNet #135](#) for further details.

REQUIRED - Insert lab-specific descriptions of PPE and hygiene practices used with Pyrophorics, including any specialized PPE (e.g., FR gloves) needed for a procedural step/task.

6. SPILL AND EMERGENCY PROCEDURES

Follow the guidance for chemical spill cleanup from [SafetyNet #13](#) and/or the [UC Davis Laboratory Safety Manual](#), unless specialized cleanup procedures are described below. Emergency procedure instructions for the UC Davis campus and UCD Medical Center are contained in the [UC Davis Laboratory Safety Manual](#) and the [Emergency Response Guide](#) (which must be posted in the laboratory). All other locations must describe detailed emergency procedure instructions below.

Once spilled, liquid or solid Pyrophoric chemicals may ignite.

The primary emergency response is to extinguish Pyrophoric fires using an appropriate extinguishing agent (dry sand, Met-L-X, soda ash or lime). Primary emergency response to extinguish Pyrophoric fires on a person would be to use an emergency eyewash/safety shower. A [flowchart graphic](#) has been provided to aid emergency response, and may be customized for each laboratory. Additional considerations for a fire involving Pyrophoric materials includes:

- A. Use an appropriate extinguishing agent (dry sand, Met-L-X, soda ash or lime) for the Pyrophoric material;
- B. Using a Class ABC fire extinguisher may be helpful to manage a lateral fire;
- C. Fire extinguishers containing water are not suitable for use in these situations; and
- D. Fire extinguishers containing water (or that may develop water over time), carbon dioxide, or halons are not suitable for fires involving organolithium compounds as they react violently.

REQUIRED - Insert descriptions of lab-specific spill clean up procedures for Pyrophorics used in this SOP. This shall include the determining criteria for small vs. large spills.

INSERT IF APPLICABLE - Descriptions of any specialized emergency procedures for locations outside of the UC Davis main campus and the UCD Medical Center campus.

If there is an unusual or unexpected occurrence when using Pyrophorics, the occurrence must be documented and discussed with the Principal Investigator or Laboratory Supervisor and others who might be using the material(s). Unusual or unexpected occurrences might include a fire, catastrophic failure, sudden rise or drop in temperature, increased rate of gas evolution, color change, phase change, or separation into layers. It is also essential that “Lessons Learned” and “Near Misses” incident reports be maintained and shared.

7. WASTE MANAGEMENT AND DECONTAMINATION

Hazardous waste must be managed according to [Safety Net #8](#) and properly labelled, using the appropriate [label](#). In general, hazardous waste must be removed from your laboratory within 9 months of the accumulation start date; refer to the [timeline for waste disposal](#). Hazardous waste pick up requests must be [completed online](#).

Decontamination:

Carefully inspect work areas to make sure no Pyrophoric materials remain. Clean contaminated work areas with wipers moistened with a dry, non-polar solvent. Be sure all ignition sources are secured before beginning cleaning up with flammable liquids. Be certain that the appropriate quenching procedure is complete before adding materials to a hazardous waste container.

REQUIRED - Insert the laboratory-specific quenching protocol(s) for the Pyrophoric(s) described in this SOP.

REQUIRED - Insert descriptions of decontamination procedures for equipment, glassware, and controlled areas (*e.g.*, glove boxes, restricted access hoods, perchloric/hot acid fume hoods, or designated portions of the laboratory).

Upon completion of work with Pyrophorics and/or decontamination of equipment, remove gloves and/or PPE to wash hands and arms with soap and water. Additionally, upon leaving a designated Pyrophoric work area, remove all PPE worn and wash hands and forearms as needed. Contaminated clothing or PPE should not be worn outside the lab. Soiled lab coats should be sent for professional laundering. Grossly contaminated clothing/PPE and disposable gloves must not be reused.

8. DESIGNATED AREA

Designated area(s) for the use and storage of Pyrophorics shall be established where limited access, special procedures, knowledge, and work skills are required. Signage indicating the materials being used and/or stored and the applicable hazards should be easily visible for the designated work space and/or storage area, for example: DANGER! PYROPHORIC MATERIALS IN USE!

REQUIRED - Insert description(s) of the designated area(s) for Pyrophorics in your laboratory. The entire laboratory, a portion of the laboratory, a fume hood, etc. can be designated.

9. DETAILED PROTOCOL

REQUIRED - Insert or attach detailed laboratory-specific procedures for the process, hazardous chemical(s), or hazard class. You may also include any relevant supporting resources (*e.g.*, SafetyNets, journal citations, etc.) that are applicable.

