**UH Guideline for Pyrophoric/Water-Reactive Chemicals**

**– Executive Summary**

The Occupational Safety & Health Administration's (OSHA) Laboratory Standard (29 CFR 1910.1450 (e) (3) (viii), requires that provisions be made for employee protection for work with Particularly Hazardous Substances (PHS). These include select carcinogens, reproductive toxins, acutely toxic substances and reactive/explosive chemicals as well as Standard Operating Procedures (SOP) relevant to safety and health considerations to be followed when laboratory work involves the use of particularly hazardous chemicals.

The UH Chemical Hygiene Plan defines work practices and procedures in order to protect students, laboratory workers, researchers, and supervisors at the University of Houston (UH) from the health and physical hazards associated with the use of hazardous chemicals. The Chemical Hygiene Plan is consistent with the U.S. Department of Labor Occupational Safety and Health Administration (OSHA) standard entitled "Occupational Exposures to Hazardous Chemicals in Laboratories" (Code of Federal Regulations, 29 CFR 1910.1450) and the Texas Hazard Communication Act (Chapter 502 of the Texas Health and Safety Code).

The purpose of the Guidelines in Chemical Hygiene Plan describe safe handling for various chemical hazard classes and some commonly-used chemicals to ensure that all laboratory personnel are adequately trained and familiar with PHS’ chemical/physical properties, health hazard information and toxicity data before their use. Procedures for containment, storage, and waste management shall be described in detail in the lab-specific SOP.

The Principle Investigator or Designee must ensure that these and other precautions designed to minimize risk of exposure to these substances are taken. The guidelines were created by the Department of Environmental Health and Safety with the goal of complying with 29 CFR 1910.1450 (e)(3)(i) and educating the campus community on the safe use of the PHS.

The Department of Environmental Health & Safety (EHS) has also established the Standard Operating Procedure (SOP) system to facilitate the creation of SOPs within the UH community. The information provided is intended to be accurate and helpful, but it should not be considered exhaustive. The provided document(s) are not comprehensive in nature and should not be considered complete until the PI completes all relevant sections. The template is provided as a tool, which can be used by the Principal Investigator (PI) to create an SOP specific to the processes present in their lab.

**UH Guideline for Pyrophoric/Water-Reactive Chemicals**

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## **Introduction**

Pyrophoric liquids and solids spontaneously ignite within 5 minutes after coming into contact with air. Water-reactive chemicals become spontaneously flammable or emit flammable gases in potentially dangerous quantities upon contact with water, steam, or moisture. The reactive nature of these chemicals makes proper training, handling, storage, and control measures critical to ensuring the health and safety of researchers. Failure to comply with safety measures can lead to fires, explosions, property damage and serious injuries or even death. This document provides guidelines for the safe use of pyrophoric and water-reactive chemicals in laboratories.

Any handling of a pyrophoric/water reactive material is high risk and must be controlled with adequate system design, direct supervision, and training. These tasks are two person tasks and workers shall not work alone.

## **Purpose and Scope**

This guideline present information on how to handle and store pyrophorics/water reactives. All UH Laboratory Personnel who work in laboratories containing pyrophorics/water reactives must familiarize themselves with this document. A copy of the signature page, the last page of this document, must be kept by the PI and Designee acknowledging Laboratory Personnel have read this document and are aware of the unique dangers and precautions that must be taken when handling the pyrophorics/water reactives.

**Overview of Hazards**

The main hazard associated with pyrophoric/water-reactive chemicals is **fire** upon contact with air or moisture in various environments including air, oxygen, water, or other chemicals with reactive hydroxyl groups. The high level of reactivity associated with these chemicals requires them to be handled in inert atmospheres, free of ignition sources.

The hazards associated with these chemicals is exacerbated by the fact that many are stored in highly flammable solvents (e.g., diethyl ether, hexane, pentane, tetrahydrofuran, etc.), further increasing the risk and severity of fires. In addition to reactivity and flammability, many of these chemicals are also classified as acutely toxic, corrosive, reproductive toxins, peroxide-forming agents or capable of damaging the liver, kidneys, and central nervous system.

**Classes of Hazards**

* Grignard Reagents: RMgX (R=alkyl or aryl, X=halogen)
* Metal alkyls and aryls: Alkyl lithium compounds; tert-butyl lithium
* Metal carbonyls: Lithium carbonyl, nickel tetracarbonyl
* Group I (Alkali) metals: Lithium, potassium, sodium, sodium-potassium alloy (NaK), rubidium, cesium, francium
* Metal powders (finely divided): Cobalt, iron, zinc, zirconium
* Metal hydrides: Sodium hydride, lithium aluminum hydride
* Nonmetal hydrides: Diethylarsine, diethylphosphine
* Non-metal alkyls: R3B, R3P, R3As; tetramethyl silane, tributyl phosphine

White and red phosphorus

## **Hazard Controls**

BEFORE working with pyrophoric/water reactive reagents, consult with your Principal Investigator (PI) to receive approval before working with highly hazardous materials, read the relevant Safety Data Sheets (SDS), technical bulletins, and guidance documents to understand how to mitigate the hazards. The SDS must be reviewed before using an unfamiliar chemical and periodically as a reminder. Perform a hazard analysis and identify the potential failures or weak points in your experimental design. Be prepared to handle accidents.

Users of reactive materials must be trained in proper lab technique stated in Standard Operating Procedures (SOP) and be able to demonstrate proficiency. Do not work alone or during off hours, when there are few people around to help. always wear the appropriate personal protective equipment.

Remove all excess and nonessential chemicals and equipment from the fume hood or glove box where pyrophoric/water reactive chemicals will be used. This will minimize the risk if a fire occurs. Keep combustible materials, including paper towels and Kimwipes, away from reactive reagents.

Keep the amount of pyrophoric/water reactive material present in your lab to the smallest amount practical. Use and handle the smallest quantity practical. It is better to o multiple transfers of small volumes than attempt to handle larger quantities (greater than about 20 mL). Alternatively, an appropriately engineered system, capable of safely handling the larger quantity must be designed, tested, and properly used.

The following controls should be considered BEFORE working with Pyrophoric/Water-Reactive Chemicals :

* *Plan and Preparation for use*
  + Only order and store the quantities of pyrophoric/water-reactive chemicals that are needed. Choose less hazardous reagents when possible.
  + All Laboratory Personnel who directly use pyrophoric/water-reactive chemicals must be hands-on trained by the PI or knowledgeable designee before using pyrophoric/water-reactive chemicals and must have undergone all general safety training requirements as well, must be documented. When under training, they shall be supervised until they are competent to use pyrophoric/water-reactive chemicals independently.
  + All Laboratory Personnel who work in the lab with pyrophoric/water-reactive chemicals, but not directly use pyrophoric/water-reactive chemicals must be in-person trained on these specific procedures by the PI or knowledgeable designee before start working in the laboratory and must have undergone all general safety training requirements as well, and must be documented.
  + All users must review SDS documents and standard operating procedures before using pyrophoric/water-reactive chemicals.
  + At least one **other** person must be present in the laboratory when pyrophoric/water-reactive chemicals are in use.
* *Engineering Controls*

The following is the set of engineering controls required when handling air/water reactive chemicals:

* **Fire Extinguishers**. Laboratory personnel working with reactive materials must have the proper equipment and the emergency phone number readily available for any emergencies, prior to starting research activities. Acceptable extinguishing media include soda ash (lime) or dry sand to respond to fires. DO NOT use water to attempt to extinguish a pyrophoric/water-reactive chemical fire as it can enhance the combustion of some of these materials, e.g. metal compounds. A small beaker of dry sand or soda ash (lime) in the work area is useful to extinguish any small fire that occurs at the syringe tip and to receive any last drops of reagent from the syringe. Review the SDS for the proper fire extinguisher to use with the given material or contact the Fire Marshal’s Office (3-5858) for assistance.
* **Eye wash and safety shower** shall be within 10 seconds walking time from the location of a hazard (approximately 55 feet). Ensure that each of these safety devices has been certified with appropriate date stamp. Bottle type eyewash stations are not acceptable.
* **Fume Hood**: Verify that the fume hood has been checked within the last 12 months. Many pyrophoric chemicals release noxious or flammable gases, and some air/water reactive chemicals are stored under kerosene. These materials must always be handled in a laboratory fume hood. Therefore, the use of a fume hood (or glove box) is required to prevent the release of flammable vapors into the lab.
* **Inert atmosphere glove boxes** are an excellent device for the safe handling of reactive materials. Glove boxes used for this purpose shall be in good working order and the moisture and oxygen levels of the atmosphere shall be confirmed prior to introduction of reactive compounds into the box. Anyone working with glove box must be trained on the standard operating procedures for the box and review these SOPs with their PI prior to beginning work.
* *Handling & Storage Precautions*

When handling pyrophoric/water-reactive chemicals, **no one shall work alone or during off hours**, when there are few people around to help.

* Use and store minimal amounts of pyrophoric/water-reactive chemicals. Do not store pyrophoric/water-reactive chemicals with other flammable materials or in a flammable liquids’ storage cabinet. Containers carrying pyrophoric/water-reactive chemicals must be clearly labeled with the correct chemical name and hazard warning at a minimum.
* Pyrophoric/water-reactive chemicals shall be handled in systems or enclosures (glove boxes) that prevent the chemicals from igniting when a dry or an inert atmosphere is required by the manufacturer or the safety data sheet.
* Pyrophoric/water-reactive shall be handled only by those with experience in their hazards and properties or under close, direct supervision by those with experience in their hazards and properties. Work with pyrophoric/water-reactive chemicals during transfer or cleanup operations requires the use of the buddy system.
* Personal Protective Equipment shall be worn as required in Section 6.0.
* Pyrophoric liquids dispensed in a chemical fume hood shall be from sure-seal-type bottles with syringes or double-tipped needles in accordance with the manufacturer’s recommendation.
* Open dispensing of pyrophoric liquids shall be done inside of an inert atmosphere glove box. Pyrophoric solids shall be handled/dispensed inside of an inert atmosphere glove box. Water reactive solids that are not protected by mineral oil or solvents shall be handled/dispensed inside of an inert atmosphere glove box.
* Residual moisture and contaminates shall be cleaned from reaction vessels, glassware, needles, and other lab equipment that will be exposed to pyrophoric reagents and water reactive materials. Equipment shall be purged with a high-purity dry inert gas prior to use.
* The void space at the top of containers of pyrophoric reagents shall be backfilled with a high-purity dry inert gas as the reagent is removed.
* Store pyrophoric/water-reactive chemicals as recommended in the SDS or product guidance. Inert gas-filled desiccators or glove boxes are suitable storage locations for most materials.
* Pyrophoric/water-reactive materials in glove boxes shall be sealed in airtight containers when the chemicals are not in use.
* If pyrophoric/water-reactive chemicals are received in a specially designed shipping, storage, or dispensing container (such as the Aldrich Sure/Seal packaging system) ensure that the integrity of that container is maintained.
* Ensure that a sufficient protective solvent, oil, kerosene, or inert gas remains in the container while the material is stored.
* **Never** return any excess chemical to the original container. Material must be used up as part of the experimental procedure or quenched using an appropriate technique as indicated in laboratory-specific SOP. Excess shall be quenched using an appropriate safe technique.
* Do not store pyrophoric/water-reactive chemicals for longer than necessary. Use chemicals as quickly as possible.
* *Personal Protective Equipment (PPE)*

The following must be worn at all times when handling pyrophoric chemicals and when working with glassware (such as a Schlenk flask) that contains pyrophoric chemicals.

* + Long pants or clothing that covers the body to the ankles and closed-toe solid top shoes must be worn when working with these compounds. A flame-resistant lab coat must be worn when working with pyrophoric chemicals. Lab coats need to be buttoned and fit properly to cover as much skin as possible. Clothing, shirt, and pants must be cotton, wool, or another natural fiber.
  + Safety glasses or goggles that meet the ANSI Z.87.1 1989 standard must be worn whenever handling pyrophoric chemicals. When there is the potential for splashes, goggles must be worn under a face shield. A face shield is also required any time there is a risk of explosion or highly exothermic reaction. All manipulations of pyrophoric chemicals which pose this risk must occur in a fume hood with the sash in the lowest or most protective position. Portable shields (i.e., blast shields), which provide protection to all laboratory occupants, shall also be used, as necessary.
  + Gloves must be worn when handling pyrophoric chemicals. Nitrile gloves may be adequate for handling small quantities of most of these in general laboratory settings. However, nitrile gloves are combustible, and heavy chemical-resistant gloves or Nomex and related aramid fiber gloves may be appropriate for working with large quantities.
  + Appropriate shoes that cover the entire foot (closed toe, closed heel, no holes in the top) must be worn at all times. For optimal protection, we strongly recommend the use of leather shoes.

**Waste Disposal**

* Never leave a container with a residue of a pyrophoric/water-reactive chemical open to the atmosphere.
* Any unused or unwanted pyrophoric/water reactive chemicals must be destroyed by transferring the materials to an appropriate reaction flask for hydrolysis and/or neutralization with adequate cooling. If you have large quantities of unreacted pyrophoric reagent material, contact EHS at 3-5858 for guidance on disposal options.
* The empty container shall be rinsed three times with an inert dry compatible solvent; this rinse solvent must also be neutralized or hydrolyzed as described below in the lab-specific procedures. The rinse solvent must be added to and removed from the container under an inert atmosphere.
* All materials (disposable gloves, wipers, bench paper, etc.) that are contaminated with pyrophoric/water-reactive chemicals must be disposed of as hazardous waste. Proper and complete Unwanted Material waste labelling of containers is vital.
* The contaminated needles, spatulas, wipes, and tools that have been in contact with pyrophoric/water-reactive chemicals shall be stored in an inert atmosphere or shall be neutralized in accordance with the manufacturer’s written instructions and the laboratory-specific instructions.
* Alert EHS for any wastes contaminated by pyrophoric/water-reactive chemicals by adding in comments during the electronic submission process.
* EHS cannot remove materials from the lab until they have been appropriately stabilized/quenched and deemed safe for transport.
* Label with EHS “Unwanted Material” Waste label that states the name/type of chemical waste & PI name.
* Unwanted Material waste labels are available for on EHS’s website at the following link. - <https://uh.edu/ehs/waste-management/labels/>
* Submit a waste request at the following link. - https://uh.edu/ehs/waste-management/
* Grossly contaminated gloves, absorbent pads, and all spill cleanup materials are hazardous waste and will be accumulated in a plastic bag and labeled as EHS Unwanted Material.

## **Exposure Procedures**

*Provide First Aid Immediately*

* If inhaled, move person into fresh air. If not breathing, give artificial respiration. Consult a physician.
* In case of skin contact, wash off with soap and plenty of water for 15 minutes. Take victim immediately to hospital. Consult a physician.
* In case of eye contact, rinse thoroughly with plenty of water for at least 15 minutes, occasionally lifting the upper and lower eyelids. Get medical aid immediately.
* If swallowed, never give anything by mouth to an unconscious person. Rinse mouth with water. Consult a physician.

*Get Help*

1. After first aid measures, seek medical attention if needed at UH Health Center on UH Main Campus or the nearest Emergency Clinics, as appropriate.
2. Call 911 on campus phone or 713-743-3333 or go to nearest Emergency Department to seek medical attention. Give details of exposure:

* Chemical name and concentration
* Amount of exposure
* Route of exposure (skin, eyes, respiratory)
* Time since exposure

1. Bring the SDS and SOP of the chemical to the Emergency Department.
2. Notify your supervisor as soon as possible for assistance.
3. Secure area before leaving. Lock doors and indicate spill if needed.

*Report Incident to Environmental Health and Safety*

1. Notify EHS immediately after providing first aid and/or getting help.
   1. During business hours (M-F/8-5) call 713-743-5858.
   2. After hours call 911 on campus phone or 713-743-3333 to be routed to EHS staff on call.
2. For all incidents and near misses, the involved person or supervisor should report to EHS at 713-743-5858.

## **Spills & Emergency Procedures**

* DO NOT use water to attempt to extinguish a reactive material fire as it can enhance the combustion of some reactive materials, e.g. metal compounds.
* Do not use combustible materials (paper towels) to clean up a spill, as these may increase the risk of igniting the reactive compound. Soda ash (powdered lime) or dry sand shall be used to completely smother and cover any small spill that occurs.
* A container of soda ash (powdered lime) or dry sand shall be kept within arm’s length when working with a reactive material.
* If anyone is exposed, or on fire, wash with copious amounts of water, except if metal compounds are involved, which can react violently with water. In the case of a metal fire, smothering the fire is a better course of action.
* Evacuate all personnel from the laboratory and restrict access. Call 9-1-1 from campus phone or 713-743-3333 for emergency assistance and for assistance with all fires, even if extinguished.
* Pyrophoric gas releases and associated fires must be extinguished by remotely stopping the gas flow. Never attempt to put out a gas fire if the gas is flowing.
* Any spill incident requires the involved person or supervisor to complete and submit the Injury Forms within 24 hours (8 hours if serious injury or hospitalization) of the incident to Risk Management.

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| **Chemical Class: Pyrophoric/Water-Reactive Chemicals**  **STANDARD OPERATING PROCEDURES**  **Type of SOP: Hazardous Class Hazardous Chemical Process**  According to the Safety Data Sheets (SDS) for Strong Oxidizers, special precautions must be taken when working with these chemicals. This Standard Operating Procedure (SOP) briefly describes the use of equipment and supplies maintained in the lab/facility, procedures that must be followed, and the responsibilities of personnel when working in these labs/facilities. PI or the designee should **amend this SOP template by entering text in the highlighted yellow area to include specifics for your lab/facility. Add *NA* if no additional lab-specific information for the Section. Users shall** not conduct experiments, even pilot studies, which are not described in this approved SOP. It is essential that all personnel follow the appropriate procedures outlined in this SOP. **Please provide the SDS associated with these chemicals to all lab personnel working with them.** |
| **PI Information**   |  |  |  |  | | --- | --- | --- | --- | | PI’s Name: | \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ | PeopleSoft ID: | \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ | | Department: | \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ | Building/Room# | \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ | |
| **1. PI Responsibilities** |
| * Perform hazard assessments, develop/approve SOPs for the hazardous chemicals and procedures; * Provide laboratory-specific training to laboratory personnel on the use of hazardous chemicals and the procedures described in this SOP and retain training records and all documentation; * Implement and enforce rules and standards concerning health and safety for laboratories; * Ensure compliance of laboratory personnel with this SOP; * Ensure the availability and enforce the use of: appropriate Personal Protective Equipment, safety equipment, emergency equipment, Safety Data Sheets (SDSs), and relevant reference materials; * Remain cognizant of chemicals stored and used in laboratories and their associated hazards; * Dispose of chemicals no longer needed by submitting an on-line waste pick up request to Environmental Health and Safety; * Provide SDS and Laboratory-specific SOP via email to [ehs@uh.edu](mailto:ehs@uh.edu) upon request. |
| **2. Chemical Information** |
| 1. List the chemical names and CAS numbers of Pyrophoric/Water-Reactive Chemicals in your lab:  |  |  | | --- | --- | | **Chemical Names** | **CAS Numbers** | |  |  | |  |  | |  |  | |  |  | |

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| **3. Engineering Controls** |
| * Please review the section on[” Engineering Controls”](#_Hazard_Controls) of UH Guideline for Pyrophoric/Water-Reactive Chemicals.   Please list the locations of the eye wash, safety shower and fume hood below.   |  |  | | --- | --- | | Type | Location (Building and Room Numbers) | | Fume Hood(s) |  | | Safety Shower (s) |  | | Glove Box (if applicable) |  | | Eyewash Station(s) |  | | Fire Extinguisher (s) |  | |

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| **4. Personal Protective Equipment (PPE)** |
| * Please review Section on [”PPE”](#_Hazard_Controls) of the UH Guideline for Pyrophoric/Water-Reactive Chemicals.   **More lab-specific information regarding PPE to train users:** |

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| **5&6. Work Practice Controls (Preparation, Handling, Storage and Transport)** |
| * Please review Section on [*“Plan and Preparation for use” and “Handling & Storage Precautions”*](#_Hazard_Controls) of the UH Guideline for Pyrophoric/Water-Reactive Chemicals.   **More lab-specific information regarding work practice to train users:** |

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| **7. Spill and Accident Procedures**  **[Specific cleaning and waste disposal procedures must be determined.]** |
| Please review Section on [*“Spills & Emergency Procedures*](#_Spills_&_Emergency)*”* of the UH Guideline for Pyrophoric/Water-Reactive Chemicals.  **More lab-specific information regarding Spill and Accident Procedures to train users:** |

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| **8. Exposure Procedures in Case of Emergency** |
| Please review Section on [*“Exposure Procedures*](#_Exposure_Procedures)” of the UH Guideline for Pyrophoric/Water-Reactive Chemicals.  **More lab-specific information regarding Exposure Procedures to train users:** |

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| **9. Waste Disposal** |
| Please review Section on *“Waste Disposal” of the* UH Guideline for Pyrophoric/Water-Reactive Chemicals.  **More lab-specific information regarding waste disposal to train users:** |

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| **10. Lab-specific Protocol/Procedure** |
| This SOP must be customized for each lab using Strong Oxidizers. Use this section to describe or attach what is being done with the chemicals, including specific laboratory procedures and quantities used. |

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| Particularly hazardous  substance involved? | X YES: | Blocks #11 to #13 are Mandatory |
| NO: | Blocks #11 to #13 are Optional. |
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| **11. Approval Required** | | |
| All staff working with Strong Oxidizers must be trained on this SOP prior to starting work. They must also be trained on the Strong Oxidizers SDS, and it must be readily available in the laboratory. All training must be documented and maintained by the PI or their designee. | | |
| **12. Decontamination** | | |
| Please indicate the decontamination methods. | | |
| **13. Designated Area** | | |
| Please indicate the designated area for storing and handling the chemicals in this SOP. | | |
| PI’s Name: | Date: | |
| Signature: | | |

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| **[Laboratory Name]**  **Documentation of Training\***  **Standard Operating Procedure for Pyrophoric/Water-Reactive Chemicals** | | | | | |
| *“I have read and understand this SOP. By signing below, I agree to fully adhere to its requirements.”* | | | | | |
| Last | First | PSID | Email | Signature | Date |
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\* This document, including the signature page with signatures by all involved personnel shall be maintained by the Principal Investigator or Designee, and be submitted to EHS either electronically via the ehs@uh.edu or hard copy upon request.

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| **Template Revision History** | | | |
| Version | Date Approved | Author | Revision Notes: |
| 1.0 | 6/18/2019 | EHLS Chemical Safety | New Guideline with Template. |
| 1.1 | 6/10/2020 | EHS Chemical Safety | Name & logo change, and review. |
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