Pyrophoric and Water-Reactive Chemicals

Introduction

Pyrophoric liquids and solids spontaneously ignite within five minutes after coming into contact with air. Water-reactive chemicals become spontaneously flammable or emit flammable gases in 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 lab personnel. Failure to comply with safety measures can lead to fires, explosions, property damage, and serious injuries. This document provides general guidelines for the safe use of pyrophoric and water-reactive chemicals in laboratories. However, the principal investigator must determine whether additional controls are required based on the application, specific chemicals being used, and other hazards associated with the research.

Hazards

The main hazard associated with pyrophoric and water-reactive chemicals is fire upon contact with air or moisture. The high level of reactivity associated with these chemicals requires them to be handled in inert atmospheres, free of ignition sources or moisture. The hazards associated with some of these chemicals are 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 toxicants, peroxide-formers, or capable of damaging the liver, kidneys, and central nervous system. Safety data sheets (SDSs) should indicate the specific hazards for the pyrophoric or water-reactive chemicals being used in the lab. Strict adherence to standard operating procedures and safe work practices must be followed to ensure safe usage.

Common Pyrophoric and Water-Reactive Chemicals

Below is a table of common pyrophoric and water-reactive chemicals. The list is not comprehensive. Be aware that the particle size, moisture, and the thermodynamics of metal oxide and metal nitride formation impacts the reactivity of many pyrophoric metals.

Pyrophoric and Water-Reactive Chemicals	
Class	**Examples**
Alkali Metals (Group 1)	Lithium, Potassium, Sodium
Alkali Metal Amides	Lithium Amide, Sodium Amide
Aluminum Compounds	Diisobutylaluminum chloride, Trimethylaluminum
Finely Divided Metals	Aluminum, Calcium, Magnesium, Titanium, Zinc
Grignard Reagents	R-Mg-X, Where R= Alkyl And X=Halogen; Butylmagnesium Chloride, Methylmagnesium Bromide, Propylmagnesium Chloride
Lithium Compounds	N-Butyllithium, Sec-Butyllithium, Tert-Butyllithium
Metal Carbonyls	Iron Carbonyl, Nickel Carbonyl
Metal Halides	Titanium (II) Chloride
Metal Hydrides	Lithium Aluminum Hydride, Potassium Hydride, Sodium Hydride
Non-Metal Hydrides	Arsine, Diborane, Dichlorosilane, Phosphine, Silane
Non-Metallic Elements	White Phosphorus
Zinc Compounds	Diethylzinc

Administrative Controls

- Safety training must be provided by the principal investigator or other qualified personnel to lab personnel working with pyrophoric and/or water-reactive chemicals. Documented training is required.
- A **Lab-Specific Standard Operating Procedure (LSOP)** must be completed, reviewed, and signed by all individuals and the principal investigator prior to working with pyrophoric or water-reactive chemicals.
- Read the safety data sheet (SDS) for each pyrophoric or water-reactive chemical prior to use.
- Eliminate, substitute less toxic chemicals, or reduce the quantities of pyrophoric or water-reactive chemicals being used if possible.

- Never work alone with pyrophoric and water-reactive chemicals.
- Perform experiments during normal business hours, if possible.
- Use argon instead of nitrogen as an inert gas, if possible, since it is heavier than air.
- Transfer multiple small volumes of pyrophoric liquids instead of a single transfer of a larger volume.
- Inspect containers and reaction vessels for signs of degradation prior to use. Replace the containers if damaged.
- Ensure glassware is dry prior to introducing pyrophoric or water-reactive chemicals.
- Review the Aldrich Technical Bulletins **AL-134** and **AL-164** prior to working with pyrophoric chemicals.

Engineering Controls

- Handle solid pyrophoric chemicals in glove box with an inert atmosphere.
- Ensure the glove box or fume hood where pyrophoric or water-reactive chemicals will be used is clear of any nonessential chemicals, combustible materials (e.g., paper towels, Kimwipes, etc.), and equipment.
- If a glove box or bag is not available, manipulation of these reagents via syringe or cannula must be conducted in a certified chemical fume hood, over a spill tray, if possible, with the sash at the lowest practicable working height.
- Needles must be equipped with locking mechanisms to prevent accidental disconnection and release of reagents.
- Use mineral oil bubblers to release excess pressure from reagent or reaction vessels.
- Never use balloons for pyrophoric chemicals.
- Place portable blast shields inside fume hoods for protection, when required.

Personal Protective Equipment

- At a minimum, wear chemical splash goggles that meet American National Standards Institute (ANSI) standard Z87.1.
- Use full face-shields over safety eyewear when highly exothermic reactions exist.
- Tie back long hair.
- Wear nitrile gloves over Nomex gloves for fire-protection purposes.
- Wear flame-resistant lab coats when working with pyrophoric and water-reactive chemicals. Lab coats must be buttoned and fit properly to cover as much skin as possible.
- Shirts, pants, and other clothing worn in labs should be cotton or wool. Synthetic clothing is strongly discouraged in laboratories where pyrophoric or water reactive chemicals are used.

- Clothing that covers the entire leg and closed-toed footwear that covers the entire foot must be worn.

Storage

- Store reactive materials as recommended in the SDS.
- Do not store reactive chemicals with flammable materials or in a flammable liquid storage cabinet.
- Store pyrophoric liquids, or compounds dissolved in liquid, in sealed containers with PTFE-lined septa to prevent air exposure.
- Ensure that sufficient protective solvent, oil, kerosene, or inert gas remains in the container, if required, during storage.
- An inert gas-filled desiccator or glove box may be a suitable storage location for most materials.
- If pyrophoric or water-reactive reagents are received in a specially designed shipping, storage, or dispensing container, ensure that the integrity of that container is maintained.
- Never return excess chemical to the original container. Small amounts of impurities introduced into the container may cause a fire or explosion.

Eyewashes and Safety Showers

- An approved eyewash station and safety shower must be immediately available within ten seconds for emergency use.
- Keep the area around the safety shower and eyewash station clear of obstructions at all times.
- Always know the exact location of your eyewash and shower and how to use all emergency equipment.
- Eyewash stations should be tested weekly by lab personnel. Facilities Operations tests safety showers annually.

Waste Management

- If pyrophoric or water reactive chemicals need to be disposed of, place a **chemical waste pick-up request** or contact **EHS**.
- In some cases, EHS may need to evaluate the materials to ensure they are safe for transport and/or disposal.

Resources

- Occupational Safety & Health Administration- **Appendix B To §1910.1200 - Physical Hazards**
- Yale Environmental Health & Safety - Standard Operating Procedure. **Pyrophoric & Water Reactive Compounds**.
- Sigma Aldrich. Technical Bulletin AL-134. **Handling Air-Sensitive Reagents**.
- Sigma Aldrich. Technical Bulletin AL-167. **Handling Pyrophoric Reagents**.