Pyrophoric Chemicals Handling and Use

Overview

Pyrophoric liquids, solids and gases are materials that may ignite spontaneously or react violently when exposed to air at or below 55 ºC (130 ºF) and must never be exposed to the atmosphere. Many pyrophoric chemicals are also water reactive. This Update provides general guidance on how to safely work with pyrophoric chemicals.

Applicability

This Update applies to all WCM laboratories that work with, handle, or store pyrophoric chemicals. It provides general hazard warning and safety precaution information to users of pyrophoric chemicals.

All laboratory personnel who work with or handle pyrophoric chemicals must be familiar with these guidelines.

Responsibilities

Principal Investigators (PIs) and Managers are responsible for:

- Identifying pyrophoric chemicals present in their laboratories and logging them in the Salute chemical inventory system;
- Implementing High Hazard Operation Procedures (HHOPs) for the safe handling and use of these materials;
- Provide appropriate personal protective equipment (PPE);
- Ensuring that employees review and understand the hazards and controls of pyrophorics prior to working with them.

Personnel who handle pyrophoric chemicals must:

- Understand the hazards associated with these materials as well as the appropriate techniques for their safe handling and use.
- Read the Sigma-Aldrich Technical Bulletins AL-134 Handling Air-Sensitive Reagents and AL-164 Handling Pyrophoric Reagents for information on safe set up, glassware preparation, disposal and clean-up.
- Complete EHS's annual Laboratory Safety Training;
- Review the approved HHOPs and receive hands-on instructions from the PI or other experienced senior laboratory staff prior to working with these materials

Environmental Health and Safety (EHS) provides assistance with the development and implementation of High Hazard Operating Procedures and associated exposure control strategies for the use of highly hazardous substances.

Procedure

HAZARD IDENTIFICATION

Review the Safety Data Sheet and product information to identify pyrophorics. Pyrophorics are typically identified on SDS with the Globally Harmonized System code ***H250 Pyrophoric liquids; Pyrorophoric solids, catches fire spontaneously if exposed to air***, with the Flame pictogram and Danger signal word.

DANGER

Examples include organo-metallic reagents (e.g., Grignard reagents), alkali earth elements (sodium, potassium, cesium), finely divided metals (Raney nickel, aluminum powder, zinc dust), metal hydrides (sodium hydride, germane, lithium aluminum hydride), alkyl metal hydrides (butyllithium, trimethylaluminum, triethylboron), metal carbonyls (nickel carbonyl, iron pentacarbonyl), gases (arsine, diborane, phosphine, silane), and silicon halides (dichloromethylsilane).

HIGH HAZARD SUBSTANCE (HHS)

Pyrophoric chemicals are High Hazard Substances and the lab must prepare a High Hazard Operating Procedure (HHOP). Refer to the EHS Update on High Hazard Operating Procedures for more details.

EMERGENCY SAFETY EQUIPMENT

An eyewash, safety shower and ABC fire extinguisher must be available within the work area and all personnel must be aware of their location prior to working with pyrophoric chemicals. **Review the chemical specific SDS prior to starting work in order to determine if specialized safety equipment is necessary.**

Weill Cornell Medicine

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EMERGENCY PROCEDURES

- **If a person is on fire:**
  - Walk the individual **calmly** to the nearest emergency shower (running may cause the fire to spread more rapidly);
  - Instruct the individual to cover their face and use the shower to extinguish the fire.
- If a person is on fire, but cannot be led to the emergency shower safely:
  - Wet the person with water, or
  - Instruct him/her to stop, drop and roll. Extinguish any small flames by patting them out using an available lab coat.
- Remove contaminated clothes & place clean, wet clothes on the burn areas. Wrap the person to avoid shock & exposure.
- Activate the nearest fire alarm pull station and call NYP EMS at 212-472-2222 for medical assistance.
- In the event of a fire in the room, activate the nearest alarm pull station and implement the R.A.C.E Procedure outlined in the Building-Specific Fire Safety Procedures.

SPILL RESPONSE

- **Call EHS at 646-962-7233 immediately for assistance. Do not attempt to handle a spill of pyrophoric chemicals.**
- Turn off all ignition sources and evacuate the laboratory immediately.

PERSONAL PROTECTIVE EQUIPMENT

Employees working with pyrophorics must wear:

Fire-resistant lab coat (e.g., Nomex®) 	Closed-toe shoes and long pants 	Face shield or goggles 	Alternative option: heat-resistant gloves (e.g., Ansell 43-113). Add nitrile or vinyl gloves for chemical protection 

STORAGE

- FDNY storage limits for storage of solid or liquid pyrophoric chemicals:
  - 1-hour fire rated lab: < 0.5 pound
  - 2-hour fire rated lab: < 1 pound.
- Store all pyrophoric chemicals under an atmosphere of inert gas or under the solvent they were shipped in.
- Store pyrophorics away from heat, flames, flammables, oxidizers, or water sources. Follow the manufacturer's guidelines.
- Never return excess chemicals to the original container as small amounts of impurities may cause a fire or explosion.

LABELING

- Label all primary and secondary containers of pyrophoric chemicals with the chemical name and hazard warning.
- The laboratory's Health and Safety Door Sign must contain appropriate warning information.
- Label the bottle with a HHOP sticker and storage area with a HHOP storage label.

HANDLING

- **Laboratory personnel are prohibited from working alone with pyrophoric chemicals.**
- Refer to the Sigma-Aldrich Technical Bulletin AL-134 Handling Air-Sensitive Reagents and AL-164 Handling Pyrophoric Reagents for proper selection of equipment and safe handling techniques.
- Do not unscrew caps from Alfa Aesar ChemSeal containers. Doing so in an ambient atmosphere will expose the chemical inside to air which may ignite pyrophoric materials.
- Use a glove box or a glove bag (e.g., AtmosBag) to handle pyrophorics if an **inert or dry atmosphere** is **required**.
- Work with pyrophorics in a chemical **fume hood** because:
  - Many pyrophoric chemicals release noxious or flammable gases;
  - Some pyrophoric materials are stored under flammable solvents, which should not be released into the lab.
- Use **safety shields** when there is a risk of explosion, splash, or a highly exothermic reaction.
- Lower the fume hood sash or use a portable shield.
- Ensure that evacuated glassware is pressure-rated as implosion can result in flying glass pieces and chemical splashes.


Atmosbag


Shlenk reaction tube

- Vacuum work involving pyrophoric chemicals must be conducted in a chemical hood or otherwise isolated. Mechanical vacuum pumps must be protected using cold traps and, where appropriate, filtered to prevent particulate release. The exhaust for the pumps must be vented into an exhaust hood. Vacuum pumps should be rated for use with pyrophoric chemicals.

Fume hood sash shielding

WASTE DISPOSAL

- All materials contaminated with pyrophoric chemicals must be disposed of as hazardous waste.
- **Unused or unwanted** pyrophoric chemicals must be completely **quenched** as part of the reaction or stabilized by transferring the materials to an appropriate reaction flask for hydrolysis and/or neutralization with adequate cooling.
- Empty containers should be rinsed three times with an inert dry solvent.
  - The rinse solvent must also be neutralized or hydrolyzed and collected and disposed via EHS.
  - The empty, rinsed container should be left open in the back of a chemical hood for at least one week.
- Alert EHS of waste contaminated by pyrophoric chemicals when placing a waste request in Salute.

References

- WCMC EHS: Laboratory Chemical Hygiene Plan
- EHS Update: High Hazard Operating Procedures
- Sigma-Aldrich Technical Bulletins AL-134 Handling Air-Sensitive Reagents and AL-164 Handling Pyrophoric Reagents
- Alfa Aesar ChemSeal Product Bulletin
- Princeton University, EHS Pyrophoric Materials
- Safe Handling of Organolithium in the Laboratory https://www.sciencedirect.com/science/article/pii/S1074909802002952 and videos http://weizman.ucsd.edu/CoursePages/Uglabs/143A_Weizman/EHS/EHS.html
- Local Law No. 26 of 2008 https://www1.nyc.gov/assets/buildings/local_laws/ll26of2008.pdf
- Sigma Chemical Company 230707 Butyllithium 2.5 M solution in hexanes