

Standard Operating Procedure

PYROPHORIC & WATER REACTIVE COMPOUNDS



This standard operating procedure (SOP) is intended to provide general guidance on how to safely work with pyrophorics and water reactive materials. This SOP is generic in nature and only addresses safety issues specific to pyrophorics and water reactive compounds. In some instances, several general use SOPs may be applicable for a specific chemical. Additional information can also be found in the University's Pyrophorics Handling Policy (ehs.yale.edu).

Pyrophoric and water reactive materials can ignite spontaneously on contact with air, moisture in the air, oxygen, or water. Failure to follow proper handling procedures can result in fire or explosion, leading to serious injuries, death and/or significant damage to facilities.

Examples of Pyrophoric/Water Reactive Materials

- 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

Potential Hazards/Toxicity

Pyrophoric and water reactive reagents ignite on contact with air and/or water and because of this they must be handled under an inert atmosphere and in such a way that rigorously excludes air/moisture. Some are toxic and many come dissolved or immersed in a flammable solvent. Other common hazards include corrosivity, teratogenicity, or peroxide formation, and may cause damage to the liver, kidneys, and central nervous system. **These compounds must not be handled while working alone.**

Users must familiarize themselves with the specific hazards and toxicity of the compounds they are working with, which can be found on the chemical's Safety Data Sheet (SDS). SDSs are available through the Safety Data Sheet link on Yale's EHS webpage (ehs.yale.edu).

Personal Protective Equipment (PPE)

The University's Personal Protective Equipment Policy can be found on the EHS website (ehs.yale.edu)

Eye Protection

Safety glasses or goggles must be worn whenever handling pyrophoric chemicals. When there is the potential for splashes, goggles must be worn under a faceshield. A faceshield is also required any time there is a risk of explosion or highly exothermic reaction. All manipulations of pyrophoric chemicals which pose this risk should 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, should also be used as necessary.

Hand Protection

Gloves must be worn when handling pyrophoric chemicals. Nitrile gloves should 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.

Skin and Body Protection

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 and water reactive chemicals. Lab coats need to be buttoned and fit properly to cover as much skin as possible. Clothing, shirt and pants, should be cotton or wool. A chemical-resistant apron worn over the lab coat is required for working with large quantities.

Engineering Controls

Fume Hood

Some pyrophoric materials are stored under flammable solvents and the use of a fume hood (or glove box) is required to prevent the release of flammable vapors into the laboratory. In addition, many reactive chemicals release noxious or flammable gases upon decomposition and should be handled in a laboratory hood. If a vacuum gas manifold system is being used to create an inert atmosphere, it must be set up inside the fume hood as well. Ensure that before any experiment involving a pyrophoric or water reactive compound begins, the fume hood is cleared of clutter and that any unnecessary potentially combustible compounds or materials have been removed.

Glove (dry) box

Glove boxes are an excellent device to control pyrophoric chemicals when inert or dry atmospheres are required. Anyone working in a glove box must be trained on the standard operating procedures for the box and review these SOPs with their Principal Investigator prior to beginning work.

Storage/Handling

- Use and store minimal amounts of air/water reactive chemicals.
- Do not store reactive chemicals with flammable materials, including inside a flammable liquids storage cabinet.
- Store reactive materials as recommended in the SDS. An inert gas-filled desiccator or glove box may be suitable storage locations for many materials.
- If pyrophoric or water reactive reagents 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 sufficient protective solvent, oil, kerosene, or inert gas remains in the container while the material is stored.
- NEVER return excess chemical to the original container. Small amounts of impurities introduced into the container may cause a fire or explosion.

Waste Disposal

Disposal of Pyrophoric Reagents

- Any container with a residue of reactive materials should never be left open to the atmosphere.
- Any unused or unwanted reactive materials must be destroyed by transferring the materials to an appropriate reaction flask for hydrolysis and/or neutralization with adequate cooling.
- The empty container should be rinsed three times with an inert dry COMPATIBLE solvent; this rinse solvent must also be neutralized or hydrolyzed. The rinse solvent must be added to and removed from the container under an inert atmosphere.
- After the container is triple-rinsed, it should be left open in back of a hood or ambient atmosphere at a safe location for at least a week.
- The empty container, solvent rinses and water rinse should be disposed as hazardous waste and should not be mixed with incompatible waste streams.

Disposal of Pyrophoric or Water Reactive Contaminated Materials

- All materials – disposable gloves, wipes, bench paper, etc. - that are contaminated with pyrophorics chemicals should be disposed of as hazardous waste.
- The contaminated waste should not be left overnight in the open laboratory but must be properly contained to prevent fires.

Emergency Procedures

Fire Extinguishers

An ABC dry powder extinguisher is appropriate for many of the reagents. However, a Class D fire extinguisher is needed if combustible metals such as sodium or potassium are used. These extinguishers must be available within 10 seconds travel time from where chemicals are being handled.

- Know the location of the nearest appropriate fire extinguisher before beginning work with the pyrophorics material.
- Anyone who works with pyrophoric material needs to be trained on the selection and use of these extinguishers by the Yale Office of Fire Code Compliance.
- A container of powdered lime (calcium oxide) or sand should be kept within arm's length when working with a pyrophoric material in a fume hood.

Fire

- If anyone is exposed, or on fire, wash with copious amounts of water at the nearest emergency shower.
- DO NOT use water to attempt to extinguish a reactive material fire.
- The recommended fire extinguisher for most reagents is a standard dry powder (ABC) type. Class D extinguishers are recommended for combustible solid metal fires (e.g. sodium, lithium aluminum hydride).
- Contact the Yale Office of Fire Code Compliance for the appropriate fire extinguisher selection and training information on its use. You may also review the SDS for assistance with fire extinguisher selection.
- Call 911 for emergency assistance and for assistance with all fires, even if extinguished.
- Pyrophoric gas releases and associated fires should be extinguished by remotely stopping the gas flow.
- Never attempt to put out a gas fire if the gas is flowing.

Eyewash/Safety Showers

An ANSI approved eyewash station that can provide quick drenching or flushing of the eyes must be immediately available within 10 seconds travel time for emergency use. An ANSI approved safety drench shower must also be available within 10 seconds travel time from where pyrophoric chemicals are used. Ensure the locations of the eyewashes and safety showers, and how to activate them, are known prior to an emergency.

First Aid Procedures

If inhaled

Remove to fresh air. Follow up with Acute Care or Employee Health as appropriate (203-432-0123).

In case of skin contact

Go to the nearest emergency shower if contaminated. Yell for assistance and rinse for 15 minutes, removing all articles of clothing to ensure contaminate is completely removed. Follow up at Acute Care/Employee Health as appropriate (203-432-0123).

In case of eye contact

Go to the nearest emergency eyewash. Yell for assistance and rinse for 15 minutes. Follow up at Acute Care/Employee Health (203-432-0123).

Spills

Small Spill

Exert extreme caution due to potential spontaneous combustion and potential ignition of flammable solvents or other materials in the area.

- Call for a co-worker to provide backup.
- Place the appropriate fire extinguisher nearby.
- Carefully remove nearby flammable materials.
- A container of soda ash (powdered lime) or dry sand should be kept within arm's length. This can be used to completely smother and cover the spill.
- Do not use combustible materials (paper towels) to clean up a spill, as these may increase the risk of igniting the reactive compound.
- Carefully quench by slow addition of isopropanol.
- After complete quench, double bag spill residues for hazardous waste pickup.

Larger Spill

Exert extreme caution due to potential spontaneous combustion and potential ignition of flammable solvents or other materials in the area.

If anyone is exposed, or on fire, rinse with copious amounts of water at the nearest emergency shower.

- Call 911 for emergency assistance.
- Evacuate the spill area.
- Post someone or mark-off the hazardous area with tape and warning signs to keep other people from entering.

Provide emergency personnel with technical advice on the chemicals involved.