Pyrophoric Standard Operating Procedure

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UNM CHEMISTRY AND CHEMICAL BIOLOGY

Researchers should not use pyrophoric reagents until they have read and fully understood these safe operating procedures. However, reading these procedures does not substitute for hands-on training. New users of pyrophoric reagents must work under the close supervision of an experienced user.

BEFORE working with pyrophoric reagents, read the relevant Material Safety Data Sheets (MSDS)/ Safety Data Sheets (SDS) and understand the hazards. The safety sheet must be reviewed before using an unfamiliar chemical and periodically as a reminder.

Procedure title	Safe Use and Handling of Pyrophoric Material
Date of creation / revision	
Name of responsible person	Principal investigator, laboratory supervisor, or autonomous researcher

1.	**This standard operating procedure (SOP) is for a**

☐ Specific laboratory procedure or experiment

Examples: synthesis of chemiluminescent esters, folate functionalization of polymeric micelles

☐ Generic laboratory procedure that covers several chemicals

Examples: distillation, chromatography

☐ Generic use of specific chemical or class of chemicals with similar hazards

Examples: organic azides, mineral acids

2.	**Chemical Description**

Pyrophoric chemicals are chemicals that ignite spontaneously in air.

The most common pyrophoric chemicals include phosphorus, alkylated metals, metal alkoxides and halides. A list of some pyrophoric chemicals is at the end of this SOP.

3.	**Risk assessment**

In general these materials are pyrophoric - they ignite spontaneously when exposed to air. They also tend to be associated with flammable solvents. Other common hazards include corrositivity, water reactivity, peroxide formation, and toxicity.

References:

http://publicsafety.tufts.edu/ehs/files/PyrophoricSOP.pdf

http://www.chemistry.ucla.edu/sites/default/files/safety/sop/SOP_Pyrophoric.pdf

4.	**Safety equipment**
4.a.	**Engineering / ventilation controls** Fume Hood Many pyrophoric chemicals release noxious or flammable gases and should be handled in a laboratory hood. In addition, some pyrophoric materials are stored under kerosene (or other flammable solvent), therefore the use of a fume hood (or glove box) is required to prevent the release of flammable vapors into

	the laboratory. Glove (dry) box Glove boxes are an excellent device to control pyrophoric chemicals when inert or dry atmospheres are required.
4.b.	**Personal protective equipment and other safety equipment** ***Eye Protection*** 1. Chemical splash goggles or safety glasses that meet the ANSI Z.87.1 1989 standard must be worn whenever handling pyrophoric chemicals. ➢ Ordinary prescription glasses will NOT provide adequate protection unless they also meet this standard. 2. When there is the potential for splashes, goggles must be worn, and when appropriate, a face shield added. 3. A face shield is required any time there is a risk of explosion, large splash hazard or a highly exothermic reaction. 4. All manipulations of pyrophoric chemicals which pose this risk should occur in a fume hood with the sash in the lowest feasible position. 5. Portable shields, which provide protection to all laboratory occupants, are advisable. ***Skin Protection*** 1. 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. 2. Heavy chemical-resistant gloves are required for working with large quantities. **3. *A flame resistant lab coat must be worn*.** 4. A chemical-resistant apron worn over the lab coat is required for working with large quantities. 5. No open toe shoes are allowed. 6. No shorts are allowed.
4.c.	**Designated area**
	Eyewash Suitable facilities for quick drenching or flushing of the eyes should be within 10 seconds travel time for immediate emergency use. Bottle type eyewash stations are not acceptable. Safety Shower A safety or drench shower should be available within 10 seconds travel time from where pyrophoric chemicals are used. Fire Extinguisher 1. A Class C dry chemical fire extinguisher must be available within 10 seconds travel time from where pyrophoric chemicals are used. 2. Know the location of the nearest Class D fire extinguisher. 3. A container of powdered lime (calcium oxide, CaO), soda ash or sand should be kept within arm's length when working with a pyrophoric material as this can be safely used to smother the flames. ➢ Users may encounter small fires at the tips of needles know to expect this, and do not panic. ➢ A beaker of sand is useful for extinguishing this —pilot lights. 4. For skin exposures, if there are no severe burns, rinse with water for 15 minutes and seek first aid. 5. Class ABC dry chemical extinguishers can be safely used for most organometallic reagents that are dissolved in organic solvents, such as T-Butyllithium in heptanes. 6. For aluminum alkyl fires involving neat reagents, use MET-L-KYL® extinguishing powder, made by Ansul, Inc. 7. If you have access to Class D fire extinguishing material, know where it is and how to use it. ➢ Typically, Class D extinguishing material is used for large quantities of fires involving combustible metals.
4.d.	Location of nearest emergency safety equipment

	Examples: organic azides, mineral acids

Item	Location
Eyewash / safety shower	
First aid kit	
Chemical spill kit	
Fire extinguisher	
Telephone	*Telephones are located near the entrance to laboratories.*
Fire alarm manual pull station	
Safety stations	

5. Transport, and storage, receiving requirements

1. Pyrophoric chemicals should be stored in a cool and dry location, under inert gas or kerosene as required.
2. Keep pyrophoric chemicals segregated from all other chemicals in the laboratory.
3. Avoid storage areas with heat/flames, oxidizers, and water sources.
4. Minimize the quantities of pyrophoric chemicals stored in the laboratory.
5. Date all containers upon receipt.
6. Containers carrying pyrophoric materials must be clearly labeled with the correct chemical name and hazard warning.

6. Protocols

Handling Pyrophoric Solid Reagents

a. Pyrophoric solids are ideally used in a sealed glove box flushed with inert gas.
b. Many pyrophoric solids are sold as solutions, or dispersions in mineral oil or are covered with hydrocarbon solvents to facilitate use.
c. Mildly pyrophoric solids (such as lithium aluminum hydride and sodium hydride) may be handled in the air for brief periods of time, but the containers must be flushed with inert gas before storage.

Transferring and Weighing Pyrophoric Solid Reagents

a. Gather all necessary experimental equipment first to avoid prolonged exposure of pyrophoric solids to air.
b. Weighing alkali metals: Cut desired piece of alkali metal under packing oil using a knife.
c. Using tweezers, transfer to adjacent flask containing toluene or heptane to rinse off oil.
d. Use tweezers again to transfer to a weighed flask of toluene and measure weight to determine mass of metal.
e. Use tweezers again to transfer to desired reaction flask.
f. AVOID low boiling rinses such as ether and pentane that tend to condense water upon evaporation.

7. Special handling procedures

1. Lithium Aluminum Hydride

a. Lithium Aluminum Hydride reacts violently with water and has a significant heat of solvation.
b. Therefore DO NOT add solvent to dry $LiAlH_4$.
c. Instead, slowly add $LiAlH_4$ to anhydrous solvent in the reaction flask.
d. The initial small amount of $LiAlH_4$ will react with any trace amounts of water.

2. Potassium metal

a. Potassium metal is considerably more reactive than lithium or sodium.
b. Potassium metal oxidizes to potassium oxide (K_2O), potassium peroxide (K_2O_2), and potassium superoxide (KO_2). The yellow peroxides are shock-sensitive and can explode when handled or cut.

c. Therefore dispose of potassium metal as hazardous waste if old or if significant amounts of yellow crust is visible.
d. The mineral oil of potassium hydride or sodium hydride dispersions can be rinsed off using a light hydrocarbon solvent such as hexane. This is easily accomplished in a glove box or can be done in a hood UNDER CAREFULLY CONTROLLED CONDITIONS.
e. Weigh out desired amount of dispersion and seal in a flask under nitrogen.
f. Add dry hexane via syringe, swirl, and let metal hydride settle.
g. Slowly syringe off hexane and then carefully discard into a separate flask containing isopropanol.
h. Repeat rinse procedure.
i. AVOID low boiling rinses such as ether and pentane that tend to condense water upon evaporation.

3. <u>Sodium amalgam, Na(Hg), (or potassium amalgam)</u>

a. Sodium amalgam, Na(Hg), (or potassium amalgam) is prepared by dissolving sodium into liquid mercury.
b. This highly exothermic process produces the intermetallic compound NaHg2 with enough heat to cause local boiling of the mercury.
c. Thus it must be performed in a hood under dry nitrogen gas.
d. The grey solid produced has the reducing potential of sodium, but is more air stable.

4. <u>Sodium Hydride (and other metallic hydrides)</u>

a. Sodium hydride is extremely reactive toward water, to the point that it will spontaneously react with moisture in air and ignite.
b. It should be treated with extreme caution as a solid pyrophoric material. It is strongly recommended that you substitute a mineral oil dispersion of sodium hydride for the —dry powder‖ form whenever possible.
c. If this substitution cannot be made, —dry powder‖ sodium hydride, or any other metallic hydride such as lithium aluminum hydride or potassium hydride, must only be manipulated in an inert atmosphere, and must never be exposed to air.
d. If a fire ever results during the use of a metallic hydride, use copious amounts of sand to smother the flames and the reagent. Never use an ABC fire extinguisher in an effort to put out a fire involving sodium hydride, as the force from the extinguisher can rapidly disperse fine powders.

8. Emergency procedures

1. emergencies (for example, fire, explosion, large-scale spill or release, compressed gas leak, valve failure)

a. **Call 911.**
b. Alert people in the vicinity and activate the local alarm systems.
c. Evacuate the area and go to emergency assembly point (EAP). *Indicate EAP here.*
d. Remain nearby to advise emergency responders.
e. Once personal safety to activate internal response.
f. Provide local notifications.

2. If personnel exposed

a. Flush contamination from eyes/skin using the nearest emergency eyewash/shower for a minimum of 15 minutes
b. Remove any contaminated clothing.
c. In the event of <u>life-threatening emergency</u>:
   i. Call 911.
   ii. Alert people in the vicinity and activate the local alarm systems.
   iii. Evacuate the laboratory and turning off ignitions sources if safe to do so.
   iv. Go to emergency assembly point (EAP).
   v. Remain nearby to advise emergency responders.
   vi. Contact SRS, UNM Police, PI, and Chemical Safety Coordinator.
   vii. Bring to the hospital copies of safety data sheets (SDSs) for all chemicals to which the victim was exposed.
d. In event of a <u>non-life threatening emergency</u>:

e. Administer first aid as appropriate.

a. Alert people in the vicinity
b. Remain nearby to advise emergency responders.
c. Contact SRS, UNM Police, PI, and Chemical Safety Coordinator.

3. For small spills / local cleanup

In the event of a minor spill or release that can be cleaned up by local personnel (personnel are authorized via work planning and control to handle spilled material, appropriate PPE is available, compatible spill response material is readily available in sufficient quantity, and cleanup is safe):

a. Notify personnel in the area and restrict access.
b. Eliminate all sources of ignition.
c. Exert extreme caution due to potential spontaneous combustion.
d. Exert extreme caution due to potential ignition of flammable solvents or other materials.
e. Call for a coworker to provide backup.
f. Place an ABC or D fire extinguisher nearby.
g. Carefully remove nearby flammable materials.
h. Powdered lime (calcium oxide, CaO) or dry sand should be used to completely smother and
i. Cover any spill that occurs.
j. Carefully quench by slow addition of isopropanol.
k. After complete quench, double bag spill residues for hazardous waste pickup.
l. Submit online waste pickup request.

1. For Large spills

a. Do not attempt to clean up, call UNM Police at 277-2241 and then SRS at 277-2753 with:
b. Location of spill/incident
c. Type of material involved and quantity
d. Injuries involved
e. Fire/explosion
f. Your location/contact information (or who to contact for further information)
g. Notify the Principal Investigator or designated Safety Officer as soon as possible also.
h. Turn off all ignition sources if this can be done safely, vacate the area and call for assistance.
i. Exert extreme caution due to potential spontaneous combustion.
j. Exert extreme caution due to potential ignition of flammable solvents or other materials.
k. Evacuate the spill area.
l. Notify the Chemical Safety Coordinator (277-2300, 277-1858)
m. Post someone or mark-off the hazardous area with tape and warning signs to keep other people from entering.
n. Provide emergency personnel with technical advice on the chemicals involved.

Building maintenance emergencies (for example, power outages, plumbing leaks)

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Additional emergency procedures

Describe additional, local emergency procedures.

9.	**Waste disposal** *Identify amounts of waste anticipated and appropriate disposal procedures. Segregate waste by hazard class (for example, flammable, corrosive) and state (solid, liquid), label appropriately, and place in the laboratory's hazardous waste cabinet.*

1. <u>Disposal of Pyrophoric Solid Reagents by Quenching</u>

a. Small amounts of unused or unwanted pyrophoric materials must be destroyed by careful quenching of the

residue. Transfer the materials to an appropriate reaction flask for hydrolysis and/or neutralization.

b. Dilute significantly with an unreactive solvent such as heptane or toluene and place the flask in an ice water cooling bath.

c. Slowly add isopropanol to quench pyrophoric materials.

d. Upon completion, add methanol as a more reactive quenching agent to ensure completion.

e. Finally, add water dropwise to make sure there are no pockets of reactive materials.

f. Dispose of as hazardous waste.

2. Alternative Quenching

a. reactive substances can be quenched by slowly adding the dilute solution to dry ice.

b. Add a mildly reactive quenching agent such as methanol.

c. AVOID low boiling diluents such as ether and pentane that tend to condense water upon evaporation.

d. Do not leave containers with residues of pyrophoric materials open to the atmosphere due to uncontrolled ignition.

3. Disposal of Pyrophoric Reagents through SRS

a. Pyrophoric solid chemicals can be disposed of as hazardous waste.

b. Carefully package and label the wastes.

c. Fill out the HMDR located at http://srs.unm.edu/hazardous-materials/hazardous-waste-collection-request.php

d. Email or fax to SRS at chemsafety@srs.unm.edu or 277-9006

Additional waste guidelines

Describe additional, local waste guidelines.

10.	**Training requirements** *List the general and laboratory-specific training required*

☐ Hazard Communication
☐ Hazardous Waste Management
☐ Glove Box Training
☐ Basic Safety Training
☐ Other: _____

Additional training requirements

List additional, local training requirements.

1. Additional training requirement

Additional training requirement

11.	**Approval** *Standard operating procedures must be approved by the laboratory manager and directorate safety coordinator.*

Laboratory manager *(name, signature, date)*: _____

Directorate safety coordinator *(name, signature, date)*: _____

Additional approvals

List subject matter experts consulted for approval:

1. Person consulted

Person consulted

Additional prior approvals required

List any tasks that require prior approval by the principal investigator or laboratory manager (for example, use of restricted chemicals and other higher hazard chemicals and running of higher hazard operations):

1. Task requiring prior approval

Task requiring prior approval

12.	**General List (not necessarily inclusive)**

- Finely divided metals (bismuth, calcium, hafnium, iron, magnesium, titanium, uranium, zirconium)
- Alkali metals (lithium, sodium, potassium, especially sodium potassiumalloy–NaK, and even more dangerous are cesium and rubidium)
- Low valent metals (titaniumdichloride)
- Nonmetals (white phosphorous)
- Metal hydrides (potassium hydride, sodium hydride, lithium aluminum hydride, uranium trihydride)
- Nonmetal hydrides (arsine, boranes, germane, phosphine, silane) (Most of these are actually gases.)
- Partially or fully alkylated derivatives of metal and nonmetal hydrides (diethylaluminiumhydride, diisobutylaluminumhydride, dichloro(methyl)silane) (Usually in liquid form or in solution.)
- Alkylated metals (butyllithium, triethylboron, trimethylaluminum) (Usually in liquid form or in solution.)
- Alkylated metal alkoxides or halides (dimethylaluminumchloride, diethylethoxyaluminium)
- Metal carbonyls (dicobaltoctacarbonyl, nickel carbonyl)Used hydrogenation catalysts, e.g. RaneyNi, are especially hazardous due to adsorbed hydrogen Copper fuel cell catalysts, e.g. Cu/ZnO/Al2O3 Methanetellurol (CH3TeH)
- Finely divided Iron sulfides (FeS, FeS2, Fe3S4), Potassium sulfide (K2S), Aluminum phosphide (AlP)