CHEM-LM-SOP-05	Revision #: 01	Implementation Date: 2021-11-05	Last Reviewed/ Update: 2021-11-05	Page #: 1 of 9

WORKING WITH PYROPHORIC COMPOUNDS

1. ***Purpose:*** to provide step by step guidance on how to use, store, and dispose of pyrophoric compounds

2. ***Scope:*** applies to all students, staff and faculty needing to use pyrophoric solids and/or liquids

3. ***Prerequisites:*** chemistry onboarding training and LM-SST must have been completed. You must contact EHS and be trained by an experienced person in your lab.

4. ***Responsibilities:*** It is the responsibility of everyone to follow the procedures described in this SOP

Personal Protective Equipment (PPE)

	Fire retardant lab coat
	Nitrile gloves
	Safety goggles (do not use prescription glasses)

	Flame-resistant/heat-proof face shield
	Blast shield (If there is reason to believe that there will be an increased risk of explosion)

5. Safe Handling Procedure:

Refer to Appendix to review special handling procedures for Lithium Aluminum Hydride, Potassium metal, Sodium amalgam Na(Hg), (or potassium amalgam), and Sodium Hydride (and other metallic hydrides).

Steps and Guidance for Safe Handling

1. Before planning any experiment, read the SDS of all the chemicals you intend on using.
2. Discuss the experiment design and risks associated with an experienced user: postdoc or PI.
3. Take note of the location of safety showers, fire extinguishers (class D) and eye-wash stations.
4. Record the experiment, H-phrases and quantities in your lab-book.
5. Remove all unnecessary chemicals (flammable or otherwise), glassware, and combustible material (such as paper) from the work area.
6. Pyrophoric materials can ignite spontaneously (within 5 minutes) on contact with air, moisture in the air, oxygen, water, or other chemicals with reactive hydroxyl groups. **Pyrophorics must be handled under an inert atmosphere that rigorously excludes air/moisture.**
7. **Work preferably in a glove box**. **If not available, always work in a fume hood**. Many pyrophoric chemicals release noxious or flammable gases and must be handled in a fume

hood or glove box. Glove boxes are an excellent device to control pyrophoric chemicals when inert or dry atmospheres are required.

8. **Keep the sash as low as possible if working in a fume hood.**
9. Keep the work area as dry as possible.
10. Do not work alone.
11. Obtain all the required materials needed to dispose of your chemical.
12. Make sure a source of inert gas is available for transfer and pressure equilibration (Schlenk line). Nitrogen might not be suitable for all pyrophorics, check SDS beforehand.
13. Use an oven to **fully dry your glassware before use**.
14. Use dry reagents.
15. Use airtight fittings with a light coat of vacuum grease (consider which solvent you are using, and that its use might dissolve the grease).
16. Use pressure rated glassware.

6. Transferring & Dispensing Pyrophoric Liquids

Small Volumes (<10 mL)

For small volumes, gas-tight syringes may be used to move liquid reagent (<10 mL) from containers if a supply of adequate inert gas is provided. It is recommended to use a long needle and a gas-tight syringe (with a PTFE plunger) that is twice the volume of liquid that will be transferred.

1. Secure both the reagent bottle and the receiving flask with a clamp.
2. Insert an inlet needle from an inert gas source into the bottle (*above the liquid level*).
3. Secure a wide gauge needle onto a syringe for transfer.
4. Flush the syringe with inert gas (repeat x3). Do not invert the bottle as such action dislodges sediments that may clog the needle.
5. Draw the required volume with the de-oxygenated syringe (*do not fill above 60%*).
6. Keeping the syringe inverted (needle up), draw a pocket of inert gas that will act as cushion before removing the needle from the reagent bottle and ensure that as little reagent as possible is present in the needle.

7. Quickly transfer to the receiving flask.
8. Note: Disposable plastic syringes larger than 20 mL are NOT appropriate for transferring pyrophoric materials. Use plastic syringes and needles only once. When used more than once, the rubber gasket of a plastic syringe may swell up leading to a jammed syringe.

High Volumes (>10 mL)

For the cannula method:

1. *Insert an inert gas inlet into the reagent bottle septum. Then, insert one end of the double-tipped cannula through into the headspace of the reagent bottle to flush the needle with nitrogen.*
2. *Insert the other end of the double-tipped needle through the septum of the reaction glassware (this apparatus must also be equipped with a gas line connected to the bubbler).*
3. *Transfer the liquid from the reagent bottle into the reaction vessel or the addition funnel by pushing down the end of the double-tipped needle in the reagent bottle into the liquid. Note: At all times during the transfer, the reaction vessel must be vented through a mineral oil bubbler and kept under a positive pressure of an inert atmosphere to prevent air from entering the system.*
4. *Once the required volume is transferred, pull up slowly on the end of the double-tipped needle in the pyrophoric reagent so that it is no longer in the liquid, but still through the septum and in the headspace above the liquid. Allow the inert gas to flow through the needle to push the trapped reagent in the needle to reaction vessel or the addition funnel.*
5. *At the conclusion of the transfer, the double-tipped needle needs to be rinsed with non-reacting solvent and the residue quenched as appropriate under an inert atmosphere (see below).*

7. Quenching Pyrophoric liquids

- Make sure that the pyrophoric residues in empty containers, spatulas, and other contaminated items are carefully quenched before disposal. After significant dilution of the residues with a non-reacting solvent under an inert atmosphere, place a cooling bath

(dry ice/acetone) under the reaction vessel to dissipate the heat, and slowly add isopropyl alcohol to quench the materials.

- Slowly add methanol followed by copious amount of water (stronger neutralization agent) to complete the quenching.

8. Waste Handling

- Never leave a container with a residue of a pyrophoric material open to the atmosphere
- Any unused or unwanted pyrophoric materials must be destroyed by following the specific destruction procedure(s). As an alternative to quenching, remember that pyrophoric chemicals can be disposed of as hazardous waste (contact EPS for guidance on disposal).
- Waste materials generated must be treated as a hazardous waste. Follow Hazardous Waste Management SOP.
- Place empty containers in the Lash Miller Chemical Waste Room and the EPS contractor will handle it during regular weekly service.
- For the empty pyrophoric containers that have secure caps for controlled access, these should be put on the 7th floor for disposal by EPS. The unrinsed empty containers must be capped.
- Do not mix with incompatible waste streams.
- Decontamination of containers in order to use them for other purposes is not permitted.

9. Storage

When storing a bottle of pyrophoric reagent for a long period of time after the initial use, the integrity of the reagent may be compromised. For example, the concentration of a solution of t-butyllithium may be higher or lower than what is given on the label; higher from solvent evaporation or lower from decomposition due to air/water infiltration.

- Purchase quantities that will be used in each experiment to avoid the storage of excessive amounts of hazardous chemicals. If storage is needed, make sure that the head space above the reagent is purged with an inert gas before storage.

- If the product was delivered in a capped bottle, periodically check the integrity of the seal.
- Limit exposure to air as much as possible.
- Keep away from heat, oxidizers, and water sources. Keep pyrophoric chemicals segregated from all other chemicals in the laboratory.
- Keep in delivery container and keep closed at all times when not in use.
- Date all containers upon receiving.
- Containers carrying pyrophoric materials must be clearly labeled with the correct chemical name and hazard warning using WHMIS workplace labels.

10. Emergency

If a spill occurred

In the event of a spill, notify lab personnel immediately that an incident has occurred. **Do not attempt to handle a large spill/reaction/fire**, or one in which you are not trained or equipped. Turn off all ignition sources **if this can be done safely**, vacate the area and call for assistance. In the event of a small spill, cover with dry sand or any non-combustible material. Do not use combustible materials (paper or cloth towel) to clean up a spill.

Laboratory emergencies should be reported to Campus Safety 416-978-2323 (non-urgent matters) or call 911 for life-threatening urgent matters. When reporting the emergency try to provide the following information:

- Location of spill/incident
- Type of material involved and quantity
- Injuries involved
- Fire/explosion
- Your location/contact information (or who to contact for further information)

In case of emergency

- If there is fire on your clothing or skin, stop-drop-and roll, unless you are within a few feet of a safety shower.

- Keep in mind that unreacted materials may reignite until they are washed off.
- If you are contaminated with a pyrophoric, remove your contaminated clothing while using the safety shower.
- Copious amounts of water will flush away the heat of reaction.
- If you have significant amounts of dry reactive compound on your body, you may brush off the bulk of it before you enter the shower, however only if it is not reacting.
- In case of eye contact, rinse thoroughly with plenty of water using an eyewash station for at least 15 minutes, occasionally lifting the upper and lower eyelids. Remove contact lenses if possible.

9. References and additional information

https://www.pnnl.gov/main/publications/external/technical_reports/PNNL-18668.pdf

https://ehs.cornell.edu/research-safety/chemical-safety/specific-chemical-hazards/pyrophoric-chemicals

https://ehs.princeton.edu/book/export/html/529

https://www.purdue.edu/ehps/rem/laboratory/HazMat/Chemical%20Materials/pyro.html

https://www.youtube.com/watch?v=YnP4VV1WB6o

https://www.youtube.com/watch?v=21iC4YEgOAs

https://en.wikipedia.org/wiki/Sheri_Sangji_case

http://www.cchem.berkeley.edu/frfgrp/images/PYR.pdf

http://chemistry.unm.edu/common/documents/pyrophoric.pdf

Appendix

Special Handling Procedures

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 LiAlH4.
c. Instead, slowly add LiAlH4 to anhydrous solvent in the reaction flask.
d. The initial small amount of LiAlH4 will react with any trace amounts of water.

Potassium metal

a. Potassium metal is considerably more reactive than lithium or sodium.
b. Potassium metal oxidizes to potassium oxide (K2O), potassium peroxide (K2O2), and potassium superoxide (KO2). 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.

Sodium amalgam, Na(Hg), (or potassium amalgam)

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.

Sodium Hydride (and other metallic hydrides)

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.

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.