CSUDH
CALIFORNIA STATE UNIVERSITY
DOMINGUEZ HILLS

Standard Operating Procedure

Pyrophorics

Print a copy of this SOP and insert into your Safety Binder.

- SOP Information

Department:	**CSUDH Campus – (Name of your department)**
Date SOP was written:	1/4/2020
Date SOP was approved by PI/lab supervisor:	Click or tap to enter a date.
Principal Investigator:	Click or tap here to enter text.
Chemical Hygiene Officer /Lab Manager:	**Ricardo Magallanes/**
Lab Phone:	**(XXX) – XXX – XXXX**
Office Phone:	**(XXX) – XXX – XXXX**
Emergency Contact:	**EHS (310) 243 – 3000** *(Name and Phone Number)*
Location(s) covered by this SOP:	**Campus** *(Building/Room Number)*

SOP Type: [☐] Specific lab procedure or experiment [☒] Generic use of specific chemical or class of chemicals w/ similar hazards [☐] Generic use of high-risk equipment

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Definitions

P.I. – Principal Investigator. Usually a professor in charge of a laboratory or set of laboratories who is actively undertaking research. They are considered the front-line supervisor and are responsible for training and personnel safety in the laboratory.

SDS – Safety Data Sheets. An essential component of the GHS and are intended to provide comprehensive information about a substance or mixture for use in workplace chemical management. Also Known as MSDS (Material Safety Data Sheet)

S.O.P. – Standard Operating Procedure. A written set of instructions that document how to safely perform work involving hazardous chemicals or hazardous operations. Includes training documentation.

1. Purpose

The purpose of this standard operating procedure is to acquaint you with the proper and safe handling, use, storage and disposal of the subject chemicals

2. Subject Chemicals Used in this Laboratory

Refer to the banded laboratory chemical inventory located in the chemical inventory program for a listing of all chemicals in this laboratory that this SOP applies to. In addition, the banded inventory includes chemical-specific notations that supplements the information provided in this SOP (e.g., special hazards, handling, PPE).

3. Properties & Hazards

Chemicals in this band are liable to ignite within five minutes after coming into contact with air. All chemicals in this band are considered highly hazardous.

The GHS and Cal/OSHA definition of the band is described in the table below:

Hazard Level	GHS Category	GHS H-Code	Cal/OSHA Definitions
Highly Hazardous	Pyrophoric Liquids/Solids (Cat.1)	H250	(none)
Generally Hazardous	All chemicals in this band are considered highly hazardous.		

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

Some examples of pyrophoric chemicals include:

- Grignard Reagents: RMgX
- Metal alkyls and aryls: *tert*-butyllithium, *n*-butyllithium, phenyllithium
- Metal carbonyls: Lithium carbonyl, nickel tetracarbonyl
- Metal powders (finely divided): Cobalt, iron, zinc, zirconium, lithium
- Metal hydrides: Sodium hydride, potassium hydride, diisobutylaluminum hydride (DIBAL-H)
- Nonmetal hydrides: Diethylarsine, diethylphosphine
- Non-metal alkyls: R_3B, R_3P, R_3As
- Phosphorus: white phosphorous
- Potassium
- Sodium
- Gases: Silane, dichlorosilane, diborane, phosphine, arsine

Many pyrophorics are sold as solutions in flammable solvents, which may exacerbate any dangerous reactions that can occur with misuse of these reagents. In addition, pyrophoric chemicals tend to exhibit additional hazards such as target organ toxicity, reproductive toxicity, corrosivity, water reactivity, and peroxide formation.

4. Administrative Control

In addition to the practices described below, follow procedures as specified in the lab-specific and special handling/use sections of this SOP.

General practices:

1. Be sure to review the Safety Data Sheet (SDS) for all chemicals to be used in the experiment.
2. **Never work alone**. At least one other person must be present in the same laboratory when any work involving hazardous chemicals is being done.
3. Eliminate or substitute for a less hazardous material when possible.
4. Design your experiment to use the least amount of material possible to achieve the desired result.
5. Verify your experimental set-up and procedure prior to use. Be familiar with the Safety Data Sheets for all chemicals in use. Assess the hazards to ensure that appropriate controls are in place to minimize risk and address emergency shut-down procedures as appropriate.
6. Consult with the PI if the work involves procedure scale-up or other large quantities or there are any questions regarding appropriate safety procedures.

5. Engineering Control

In addition to the practices described below, follow procedures as specified in the lab-specific and special handling/use sections of this SOP.

General practices:

1. In general, it is preferable to perform all work with hazardous chemicals in a fume hood. Sash height should be kept as low as possible to avoid the escape of vapors, gases and particulates.
2. Supplemental equipment such as blast shields should be used when working with chemicals or processes that may result in explosions or pressure releases.
3. Consider the use of a glove box, toxic gas cabinet or other local exhaust in order to further contain hazards as appropriate.

Band-specific practices:

1. Fume Hoods. All work with pyrophoric materials must be conducted in a fume hood or other type of enclosed and ventilated provision as discussed below.
2. Glove Boxes. Glove boxes are an excellent device to control pyrophoric chemicals when inert or dry atmospheres are required.
3. Inert Atmosphere Manifold (Schlenk Line). Nitrogen or argon lines are extremely useful when performing manipulations of air- and/or water-sensitive reagents. If a glove box cannot be used, proper use of an inert atmosphere manifold can help minimize exposure of these reagents to air and water.

4. Gas Cabinets. Storage of pyrophoric gases is described in the California Fire Code, Chapter 41. Gas cabinets, with appropriate remote sensors and fire suppression equipment, are required. Gas flow, purge and exhaust systems should have redundant controls to prevent pyrophoric gas from igniting or exploding. All pyrophoric gases must have Restricted Flow Orifices (RFO) installed on the cylinder. Emergency back-up power should be provided for all electrical controls, alarms and safeguards associated with the pyrophoric gas storage and process systems.

6. Personal Protective Equipment

In addition to the practices described below, follow procedures as specified in the lab-specific and special handling/use sections of this SOP.

Respiratory Protection

Respiratory protection is generally not required for lab research, provided the appropriate engineering controls are employed. Respirators should be used only under any of the following circumstances:

Lab personnel intending to use/wear a respirator mask must be trained and fit-tested by EH&S. This is a regulatory requirement. If you think that your process may require respirator use, contact EH&S for assistance.

Hand Protection

Disposable nitrile gloves provide sufficient protection for most routine lab operations involving small quantities. They should be changed if liquid is splashed onto them. They are not appropriate for longer operations or operations using larger quantities.

For longer operations, or operations using larger quantities, use thicker gloves made from a material appropriate for the specific chemical in use (e.g., natural rubber, butyl, neoprene, nitrile, PVA).

When working chemicals or processes that increase the risk of exposure to fire, use hand protection appropriate to both the risk of chemical exposure and the risk from fire. The use of an outer chemical resistant glove and an inner fire resistant (FR) inner glove/liner is permitted to provide flexibility in choosing effective gloving options when both types protection are needed.

Gloves must be inspected prior to use for signs of wear or damage. FR gloves/liners that have been exposed to reagent or fire should not be re-used. Such gloves should be disposed of in accordance with appropriate laboratory disposal practices.

Use proper glove removal technique (without touching glove's outer surface) to avoid skin contact with any chemical residues on the surface. Wash and dry hands after use.

For additional information on selection of glove material, review the specific chemical Safety Data Sheet. Consult with your preferred glove manufacturer's website to ensure that the gloves you plan on using are compatible with a specific chemical substance. Common manufacturer glove selection guidance can be found at:

Chemical Resistance:
http://www.ansellpro.com/download/Ansell_8thEditionChemicalResistanceGuide.pdf
http://www.allsafetyproducts.biz/page/74172
http://www.showabestglove.com/site/default.aspx

http://www.mapa-pro.com/our-gloves/protections/chemical-protection/b/handled_product.html

Eye Protection

Use tightly fitting safety goggles whenever working in the laboratory. A face shield is also recommended.

Skin and Body Protection

Long pants, closed toed-shoes, shirt and a lab coat must be worn whenever working in the laboratory. Flame resistant Nomex® lab coats should be used when working with chemicals or processes that increase the risk of fire. Fully extend sleeves to the wrists and keep buttoned at all times. Avoid wearing synthetic clothing when practicable.

Hygiene Measures

Wash hands immediately and thoroughly after handling chemicals. Any contaminated clothing should be disposed of or washed before reuse.

Band-specific practices:

1. Flame resistant Nomex® lab coats must be worn when using highly flammable chemicals.
2. No synthetic clothing may be worn when using highly flammable chemicals with an open flame.
3. When handling a liquid pyrophoric material outside of an inert atmosphere glove box, hand protection must include an appropriate chemical resistant outer glove and an approved fire resistant (FR) inner glove/liner. When appropriate for the necessary chemical resistance, the outer gloves should be made of a self-extinguishing material such as neoprene.

7. Special Handling & Storage Requirements

In addition to the practices described below, follow procedures as specified in the lab-specific section of this SOP.

Band-specific practices:

1. Storage of pyrophoric chemicals:
    a. Pyrophoric reagents must be handled and stored in a manner to avoid exposure to atmospheric oxygen and moisture.
    b. Do not store pyrophoric chemicals with flammable materials or in a flammable liquids storage cabinet. Containers carrying pyrophoric materials must be clearly labeled with the correct chemical name, in English, and hazard warning.
    c. Desiccators or glove boxes are commonly suitable for storage location of pyrophoric chemicals.
    d. If pyrophoric reagents are received in a specially designed shipping, storage or dispensing container, ensure that the integrity of that container is maintained.
    e. Ensure that sufficient protective solvent, oil, kerosene, or inert gas remains in the container while the material is stored.
    f. NEVER return excess chemical to the original container. Small amounts of impurities introduced into the container may cause a fire or explosion.
    g. For storage of excess chemical, prepare a storage vessel in the following manner:

i. Dry a new empty containers thoroughly
ii. Select a septum that fits snugly into the neck of the vessel
iii. Insert septum into neck in a way that prevents atmosphere from entering the clean, dry (or reagent filled) flask.
iv. Insert a needle to inject inert gas and to maintain a blanket of dry, inert gas above the reactive reagent and quickly insert a second needle to vent the flask.
v. Once the vessel is fully purged with inert gas, remove the vent needle and add the reagent carefully, then remove the gas line.
vi. For long-term storage, the septum should be secured with a copper wire.

2. Working with pyrophoric reagents:
   a. Never work alone. At least one other person must be present in the same laboratory and must be informed when any work involving pyrophoric reagents are carried out.
   b. Finely divided pyrophoric solids must be transferred under an inert atmosphere in a glove box. Liquids may be safely transferred employing proper syringe, cannulation, or Schlenk techniques and equipment as discussed in the Aldrich Technical Information Bulletin AL-134: http://www.sigmaaldrich.com/content/dam/sigma-aldrich/docs/Aldrich/Bulletin/al_techbull_al134.pdf.
   c. Pyrophoric gases should be handled in compliance with the California Fire Code, Chapter 41.
   d. If possible, run reactions involving pyrophoric reagents in an inert atmosphere glove box.
   e. If a glove box cannot be used, it is better to do multiple transfers of small volumes than to attempt to handle larger quantities. Consider using the cannulation method when transferring more than 20 mL.
   f. Make sure the area where the experiment is being performed has been adequately prepared for the experiment.
   g. Designate a fume hood or glove box for hazardous work.
   h. Keep combustible materials, including paper towels and Kimwipes, away from pyrophoric reagents.
   i. Remove all excess and nonessential chemicals and equipment from the fume hood or glove box where pyrophoric reagents are in use.
   j. A container of powdered lime or dry sand should be kept within arm's length when working with a pyrophoric material, which may be adequate to smother a small spill that might occur and to receive any last drops of reagent from the syringe

8. First Aid

In addition to the practices described below, follow procedures as specified in the lab-specific and special handling/use sections of this SOP.

Consult the Safety Data Sheet for the subject chemical for specific first aid procedures. General first aid procedures for hazardous chemicals are provided below.

If inhaled
Move to fresh air. Have victim rest in half-upright position. Artificial respiration victim is not breathing. Seek medical attention immediately.

In case of skin contact

In case of contact, immediately flush skin with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Wash clothing before reuse. Thoroughly clean shoes before reuse. Get medical attention immediately

In case of eye contact
Check for and remove any contact lenses. In case of contact, immediately flush eyes with plenty of water from emergency eyewash station for at least 15 minutes. Get medical attention immediately.

If swallowed
If swallowed, do not induce vomiting unless directed to do so by medical personnel. Never give anything by mouth to an unconscious person. Loosen tight clothing such as a collar, tie, belt or waistband. Get medical attention immediately.

9. Medical Emergency

Be familiar with information in the CSUDH Emergency poster.

a. Life Threatening Emergency (all times: Business Hours, After Hours, Weekends and Holidays)--CALL 911 if the condition is LIFE THREATENING or REQUIRES IMMEDIATE MEDICAL ATTENTION. *Note: All serious injuries must be reported to EH&S at* **ext. 2895** *within 8 hours.* Complete online incident report at https://www.csudh.edu/Assets/csudh-sites/rm-ehos/docs/risk-management-ehos/accident-report-form-std-268.pdf

b. Non-Life Threatening Emergency – Notify your supervisor or faculty staff if condition is not life threatening or does not require immediate medical attention.

ALL WORK RELATED INJURIES MUST BE REPORTED via the On-line Incident Form https://www.csudh.edu/hr/workers-compensation/ **or call Human Resources, Workers Compensation (310) 243-3771.**

10. Spill & Accident Procedures

In addition to the practices described below, follow procedures as specified in the lab-specific and special handling/use sections of this SOP.

Evacuate the spill area. Post someone or mark-off the hazardous area with tape and warning signs to keep other people from entering the area. Keep the appropriate fire extinguisher nearby. Avoid incompatible extinguishing agents. Use Class A-B-C or B-C for flammable liquids. **Fire extinguishers containing water are not suitable for flammable liquid fires.**

Spill – Assess the extent of danger. Help contaminated or injured persons if safe to do so. Evacuate the spill area. Avoid breathing vapors. If possible, confine the spill to a small area using a spill kit or absorbent material. Keep others from entering contaminated area (e.g., use caution tape, barriers, etc.).

Small (<1 L, <100 g) – If you have training, you may assist in the clean-up effort. Use appropriate personal protective equipment and clean-up material for chemical spilled. Double bag spill waste in clear plastic bags, label and take to the next chemical waste pick-up.

Large (>1 L, >100 g) – Dial **911** and EH&S at **ext. 3000** for assistance.

Chemical Spill on Body or Clothes – Remove clothing and rinse body thoroughly in emergency shower for at least 15 minutes. Seek medical attention. *Notify supervisor and EH&S at* **ext. 3000** *immediately.*

Chemical Splash Into Eyes – Immediately rinse eyeball and inner surface of eyelid with water from the emergency eyewash station for 15 minutes by forcibly holding the eye open. Seek medical attention. *Notify supervisor and EH&S at* **ext. 3000** *immediately.*

Band-specific practices:

1. A small beaker of dry sand or soda ash (lime) in the work area is useful to extinguish any small fire that occurs at the syringe tip and to receive any last drops of reagent from the syringe.

2. **DO NOT** use a carbon dioxide fire extinguisher or water to attempt to extinguish a pyrophoric material fire as these types of extinguishers can actually enhance the combustion of some pyrophoric materials. The recommended fire extinguisher is a standard dry powder (ABC) type and should be within immediate reach in the event of an incident. Class D extinguishers are recommended for combustible solid metal fires (e.g. sodium), but not for organolithium reagents.

3. **DO NOT** use water on a pyrophoric reagent fire, as it can make the incident even worse.

4. Do not use combustible materials like paper towels to clean up a spill, as these may increase the risk of ignition with a pyrophoric reagent. Soda ash (powdered lime) or dry sand may cover and contain any small spill that occurs.

11. Decontamination & Waste Disposal Procedure

In addition to the practices described below, follow procedures as specified in the lab-specific and special handling/use sections of this SOP.

All of the subject chemicals must be disposed as a hazardous waste.

Label Waste

- Hazardous waste labels must be placed on the hazardous waste container upon the start of accumulation.

Store Waste

- Hazardous waste containers must be kept closed, except when adding waste.
- Hazardous waste containers must be stored in secondary containment to adequately contain all of the contents of the container.
- Hazardous waste containers must be inspected weekly for signs of leaks, corrosion, or deterioration.

Dispose of Waste

- Hazardous waste must be transferred to EH&S for disposal within 6 months of being generated.
- Empty Containers: At no time should full or partially full containers be placed in the trash.
- Hazardous Waste Disposal:
    - Visit: https://www.csudh.edu/ehs/environmental/hazardous-waste
    - Fill out the “CSUDH Hazardous Waste Label”
    - EH&S will pick up your waste within 1-3 days.
- **Do not** dispose of chemicals by pouring them down the drain or placing them in the trash.

- **Do not** use fume hoods to evaporate chemicals.

12. Safety Data Sheet (SDS) Location

Online SDSs can be accessed at **http://hq.msdsonline.com/csuedusl**

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13. Required Travel/Approvals

In addition to the practices described below, follow procedures as specified in the lab-specific and special handling/use sections of this SOP.

All work with the subject chemicals requires the following prior to beginning work:

1. Must be pre-approved by the Principal Investigator prior to use and all training must be well documented.
2. Must be familiar with the CSUDH Chemical Hygiene Plan. https://www.csudh.edu/ehs/health-safety-programs-policies/
3. Must have documented Laboratory Safety training.
4. Must read the relevant Safety Data Sheet (formerly referenced as **M**aterial **S**afety **D**ata **S**heets).
5. Any additional laboratory specific training that is needed is referenced in the 'Laboratory Specific Use Procedures' section. Signed and dated training documents must be uploaded into each assigned researchers training records.

14. Additional Notes

Any deviation from this SOP requires approval from **P.I.**

15. Documentation of Training

- Prior to conducting any work with the subject chemicals, designated personnel must provide training to his/her laboratory personnel specific to the hazards and procedures involved in working with these substances.
- The Principal Investigator must provide his/her laboratory personnel with a copy of this SOP and a copy of the SDS provided by the manufacturer.
- The Principal Investigator must ensure that his/her laboratory personnel have attended appropriate laboratory safety training or refresher training within the last one year.

I have read and understand the content of this SOP:

Name	Signature	CSUDH ID #	Date

16. Lab Specific Procedures

The following describe how the subject chemicals are used in this laboratory beyond the practices described above.

This section must describe lab-specific procedures to address the safe use of all highly hazardous chemicals from this band in use in the laboratory. These procedures may be organized around specific chemicals, specific tasks or the band as a whole. The following minimum requirements must be met:

- Identify designated use areas within the laboratory for highly hazardous chemicals in the following hazard bands:
  - Carcinogens
  - Reproductive Toxins
  - Toxic Chemicals
- Identify maximum use quantities for which the procedures in this band apply.
- If it is determined that this hazard band SOP is sufficient to address the safe use of all subject chemicals in this lab, then include the following statement in this section: *"Procedures described in this hazard band SOP are sufficient for addressing the safe use of subject chemicals in this laboratory within the listed quantity limitations."*
- If it is determined that this hazard band SOP is not sufficient to address the safe use of all chemicals from that band in the lab, then write lab-specific procedures for to address these high hazard operations. Such operations are generally indicated by:
  - tasks requiring the use of specialized PPE,
  - tasks using highly hazardous chemicals outside of the fume hood,
  - tasks using larger quantities of hazardous chemicals,
  - tasks involving the use of particular chemicals considered by CSUDH EHS to be extremely hazardous, and
  - tasks considered to present high risk by lab personnel.

A few examples of what lab-specific tasks may look like are provided below:

Task #1: Title of the specific procedure being done.

1) Provide step-by-step instructions in a numbered/lettered format.
2) Include in the procedure any relevant:
   a) Locations of "designated areas" as called for in the special handling section of the SOP, or as otherwise required by regulations. *The entire laboratory, fume hood, or a portion of the laboratory may be considered as a designated area.*
   b) Use of specific administrative, engineering and PPE controls.
   c) Specific quantity use limits/restrictions.
   d) Specific storage requirements.
   e) Specific first aid and spill procedures (including what should be handled by whom).
   f) Specific disposal procedures.
   g) Process-specific PI approvals required.

Task #2: Making dilutions of the acids and bases.

1) Consult with PI and obtain approval if quantities greater than 4 L are needed.
2) In a fume hood, add the appropriate amount of concentrated acid or base to the calculated amount of water.
3) Return the concentrated acids/bases to the proper secondary containment or cabinet.

Task #3: Using the pH meter.

1) Calibrate on the day of pH testing using at least 2 standards.
2) Before use, rinse the electrode with deionized water and blot dry with a kim-wipe.
3) Transfer the electrode to the test solution.
4) If using a stir plate, make sure the electrode does not touch the stir bar.
5) Record the pH when the reading is stable (5–20 seconds after insertion of the electrode into the solution)
6) Add dilute acid or dilute base drop-wise until the correct pH is reached.
7) Rinse the electrode with deionized water and store according to the manufacturer's instructions.
8) Make sure the acid and base caps are on tightly.

Add as many tasks as necessary.