Pyrophoric Chemicals SOP

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1. SCOPE

This guideline identifies general safety precautions that should be reviewed and followed when working with pyrophoric chemicals at UNM. Pyrophoric liquids, solids, and gases are materials that may ignite or react violently when exposed to air. Many pyrophoric chemicals are also water-reactive.

1.1. Common Pyrophorics Used in Labs:

- Alkali metals (lithium, sodium, potassium)
- Phosphorus (white)
- Organic-metallics (tributylaluminum, tert butyllithium)
- Finely divided metals (zirconium, titanium)
- Metal carbonyls (pentacarbonyl iron, nickel carbonyl)
- Alkylated, metal alkoxides, or non-metalhalides (diethylethoxyaluminum, dichloro(methyl) silicone)

2. RESPONSIBILITIES

2.1. Environmental Health & Safety (EHS) is responsible for:

- Preparing, reviewing and periodically revising this program.
- Monitoring compliance with this program.
- Providing general pyrophoric materials safety training.
- Reviewing and approving procedures for all controlled, highly toxic, or highly hazardous gases.
- Determining health hazard classifications for previously unlisted gases, including acute and chronic toxicity, carcinogenicity, flammability, pyrophoricity and corrosivity.
- Conducting exposure assessments and evaluating exposure control measures.
- Providing or coordinating emergency response for chemical spills.
- Investigating accidents.
- Maintaining employee occupational exposure assessment records.

2.2. Deans, Directors, and Department Heads are responsible for:

- Ensuring departmental compliance with all the procedures outlined in this program.

2.3. Supervisors and/or PI's are responsible for:

- Ensuring compliance with this program in their work area(s).
- Developing Standard Operating Procedures (SOPs) that address the lab-specific safety measures to be implemented when using pyrophoric gases.

- Ensuring employees working around pyrophoric materials receive the appropriate training.
- Coordinating the provision of medical examinations, exposure monitoring and record keeping.
- Arranging for immediate emergency response, if necessary, for chemical spills, injuries and overexposures.
- Maintaining a Safety Data Sheet (SDS) for all pyrophoric materials used in the work area.

2.4. Employee Occupational Health Services (EOHS) is responsible for:

- Maintaining records of physical examinations, x-rays and tests.

2.5. Employees and Researchers are responsible for:

- Knowing the provisions of the Pyrophoric Materials SOP.
- Reporting accidents, possible exposures or unsafe conditions to their supervisor.
- Following SOPs and proper safety protocols when using pyrophoric chemicals.
- Utilizing engineering controls, administrative controls, and PPE.

3. General Safety Procedures

3.1. Engineering Controls

3.1.1. Fume Hood

Many pyrophoric materials 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.

3.1.2. Glove (dry) box

A glove box may be used with pyrophoric material if an inert environment is required. The lab Principal Investigator and/or designated Safety Officer are responsible for ensuring that staff are trained and competent in using a glove box. If the potential exists for an explosion or a high thermal reaction, additional shielding should be utilized. This may involve the use of shielding in a glove box or in the case of a fume hood with the sash in the lowest possible position. Portable shields may also be used for additional protection.

3.2. Administrative Controls

All users of pyrophoric materials must take the Laboratory Safety course in Learning Central (course # SRS WB 002) before working in the lab. Users must be trained thoroughly by a qualified and experienced supervisor on techniques for handling pyrophoric materials, and

must be directly supervised when first starting with these techniques. Also, users must consult with the PI and obtain approval when working with highly hazardous materials.

3.2.1. Safe Work Practices

1. DO NOT WORK ALONE when using pyrophoric materials. Other members in the lab should be notified of the use of pyrophoric materials in advance so that they are ready to help in case of accidents.
2. Consider performing a "dry run" to identify and resolve possible hazards before conducting the actual procedure.
3. Keep combustible materials (paper towels cardboard, clothing) away from pyrophoric materials.
4. Minimize the quantity of pyrophoric materials used and stored.
5. It is better to do multiple transfers of small volumes than attempt to handle larger quantities. Consider using the cannula method when transferring more than 20 mL of liquid pyrophoric material.

3.3. Personal protective equipment

3.3.1. Eye Protection

1. Chemical splash goggles or safety glasses that meet the ANSI Z.87.1 1989 standard must be worn whenever handling pyrophoric materials. 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 materials 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.

3.3.2. Skin Protection

1. Gloves must be worn when handling pyrophoric materials.
    a. 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 while handling pyrophoric materials.
4. A chemical-resistant apron worn over the lab coat is required for working with large quantities.
5. No open-toe shoes are allowed.

3.4. Designated area

All work involving pyrophoric chemicals must be performed in a designated area of the lab. The designated area should be known to all laboratory members and contain the equipment listed below.

3.4.1. 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.

3.4.2. Safety Shower

A safety or drench shower should be available within 10 seconds travel time from where pyrophoric materials are used.

3.4.3. Fire Extinguisher

1. A Class D 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.
    a. Users may encounter small fires at the tips of needles - know to expect this and do not panic.
    b. A beaker of sand is useful for extinguishing small fires at the tips of needles.
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.
    a. Typically, Class D extinguishing material is used for large quantities of fires involving combustible metals.

4. Special Handling Requirements

4.1. Ergonomic Considerations

Glove boxes can offer benefits with regards to lab personnel safety. However, they can also be uncomfortable for the following reasons:

- Arms remain extended for long periods of time.
- The thick gloves may make the user overcompensate on grip strength.

- Lab personnel using glove boxes should follow these steps to make glove box use more comfortable:
    - Reduce side reaching by moving all materials from the transfer chamber to the main chamber at one time.
    - Utilize antifatigue matting or use a sit-stand seat.
    - Take frequent stretch breaks.

4.2. Special Handling Procedures

4.2.1. Lithium Aluminum Hydride

Lithium aluminum hydride reacts violently with water and has a significant heat of solvation; therefore DO NOT add solvent to dry LiAlH4. Instead, slowly add LiAlH4 to anhydrous solvent in the reaction flask. The initial small amount of LiAlH4 will react with any trace amounts of water.

4.2.2. Potassium metal

Potassium metal is considerably more reactive than lithium or sodium. 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. Therefore dispose of potassium metal as hazardous waste if old or if significant amounts of yellow crust. 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. Weigh out desired amount of dispersion and seal in a flask under nitrogen.

1. Add dry hexane via syringe, swirl, and let metal hydride settle.
2. Slowly syringe off hexane and then carefully discard into a separate flask containing isopropanol.
3. Repeat rinse procedure.
4. AVOID low boiling rinses such as ether and pentane that tend to condense water upon evaporation.

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

If this method is used all precautions for mercury exposure should be taken. Mercury is a neurotoxin and should be handled with extreme caution. See SDS for elemental mercury for more information.

Repeat rinse procedure listed in section 4.2.2. Sodium amalgam, Na(Hg), (or potassium amalgam) is prepared by dissolving sodium into liquid mercury. This highly exothermic process produces the intermetallic compound $NaHg_2$ with enough heat to cause local boiling of the mercury. Thus it must be performed in a hood under dry nitrogen gas. The grey solid produced has the reducing potential of sodium, but is more air stable.

4.2.4. Sodium Hydride (and other metallic hydrides)

Sodium hydride is extremely reactive toward water, to the point that it will spontaneously react with moisture in air and ignite. 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. 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.

5. Transportation & Storage

1. Pyrophoric chemicals should be stored in a cool and dry location, under inert gas or kerosene or as required by the manufacturer.
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 material stored in the laboratory.
5. Date all containers upon receipt and periodically check the condition of the container and material.
6. Containers carrying pyrophoric materials must be clearly labeled with the correct chemical name and hazard warning.

6. Emergency Procedures

In the event of a spill or adverse reaction, notify lab personnel immediately that an incident has occurred. Do not attempt to handle a large spill/reaction/fire or any incident which you are not trained or equipped for. Turn off all ignition sources if this can be done safely, vacate the area and call for assistance.

In the event of emergency (e.g. fire, explosion, large-scale spill or release, compressed gas leak, valve failure) follow the procedure listed below.

1. Call 911.
2. Alert people in the vicinity and activate the local alarm systems.
3. Evacuate the area and go to emergency assembly point (EAP).
4. Remain nearby to advise emergency responders.
5. Provide local notifications.

6.1. In Case of Exposure

1. Flush contamination from eyes/skin using the nearest emergency eyewash/shower for a minimum of 15 minutes.
2. Remove any contaminated clothing.
3. *In the event of life-threatening emergency:*
    a. Call 911.
    b. Alert people in the vicinity and activate the local alarm systems.
    c. Evacuate the laboratory and turning off ignitions sources if safe to do so.
    d. Go to emergency assembly point (EAP).
    e. Remain nearby to advise emergency responders.
    f. Contact EHS, UNM Police, PI, and Chemical Safety Coordinator if applicable.
    g. Bring to the hospital copies of safety data sheets (SDSs) for all chemicals to which the victim was exposed.
4. In event of a non-life threatening emergency:
    a. Administer first aid as appropriate.
    b. Alert people in the vicinity.
    c. Remain nearby to advise emergency responders.
    d. Contact EHS, UNM Police, PI, and Chemical Safety Coordinator.

6.2. Laboratory Emergency Reporting

Laboratory emergencies should be reported to the UNM Police at (505) 277-2241 and then UNM Environmental Health & Safety at (505) 277-2753. Communicate the following:

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

Notify the Principal Investigator or designated Safety Officer as soon as possible.

7. SPILLS

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):

1. Notify personnel in the area and restrict access.
2. Eliminate all sources of ignition.
3. Use extreme caution due to potential spontaneous combustion.
4. Use extreme caution due to potential ignition of flammable solvents or other materials.
5. Call for a coworker to provide backup.

6. Place an ABC or D fire extinguisher nearby.
7. Carefully remove nearby flammable materials.
8. Powdered lime (calcium oxide, CaO) or dry sand should be used to completely smother and cover any spill that occurs.
9. Carefully quench by slow addition of isopropanol.
10. After complete quench, double bag spill residues and place a label on the bag that lists all contents of the bag.
11. Submit an online waste pickup request to EHS.

7.1. For Large spills

1. Do not attempt to clean up -- call UNM Police at (505) 277-2241 and then EHS at (505) 277-2753 with information listed in Laboratory Emergency Reporting.
2. Turn off all ignition sources if this can be done safely, vacate the area and call for assistance.
3. Use extreme caution due to potential for spontaneous combustion or ignition of flammable solvents.
4. Notify the Chemical Safety Officer, if applicable.
5. Post someone or mark-off the hazardous area with tape and warning signs to keep other people from entering.
6. Provide copies of SDSs to emergency personnel.

7.2. Spill Reporting

All spills should be reported to Environmental Health & Safety at (505) 277-2753. Large spills should be reported to the UNM Police at (505) 277-2241. Communicate the following:

1. Location of spill/incident
2. Type of material involved and quantity
3. Injuries involved
4. Your location/contact information (or who to contact for further information)
5. Notify the Principal Investigator or designated Safety Officer as soon as possible.

8. Decontamination Procedures

Cleanup and decontamination may require the use of activated carbon adsorbent or other nonreactive material. Review the SDS for additional guidance.

9. Disposal

Handling and disposal of pyrophoric chemicals should be done in accordance with the lab protocol established by the Principal Investigator (PI). Removal of potentially pyrophoric material from a glove box may involve placing material in a zip-lock bag or quenching material or placing the material under oil/water. The PI or designated Safety Officer must ensure that

these procedures are clearly communicated and that the supplies necessary are available prior to use of the pyrophoric.

Waste disposal requests should be directed to EHS at (505) 277-2753.

10. EMPLOYEE INFORMATION AND TRAINING

Supervisors are responsible for ensuring that employees with potential exposure to a pyrophoric material receive the appropriate training before working with it. All training must be documented by the individual presenting the training session or through Learning Central. Supervisors should review this information with employees annually.

At a minimum, training must include:

- Laboratory Safety (online course SRS WB 002 in Learning Central)
- UNM Chemical Hygiene Plan
- Lab-specific SOPs

11. SOURCES

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

https://yvesrubin.files.wordpress.com/2011/02/1-pyrophoric-reagents.pdf