

**Applies to:** (examples; Faculty, Staff, Students, etc)

Faculty , Staff , Students

**Policy Overview:**

Issued: 10-01-2017

Next Review Date: 07-19-2022

Frequency of Review: Annually

Pyrophoric and water-reactive materials can ignite spontaneously on contact with air, moisture in the air, oxygen, or water and therefore atmospheric exposure must be limited appropriately for the risk posed by the material employed. These materials can be found in solid, liquid, or gas form. Table 1 lists common classes of chemicals that fall into this category. Inattention to proper handling procedures outlined by the University and laboratory standard operating procedures (SOPs) can result in fire or explosion, culminating in serious personal injuries, death and/or significant damage to facilities. Any handling of a pyrophoric/water-reactive material is high risk and must be controlled with adequate engineering controls, direct supervision, and documented training.

**Definitions:**

<u>Term</u>	<u>Definition</u>
Pyrophoric	Liable to ignite spontaneously on exposure to air

**Details:**

1. Classes of pyrophoric agents

- a. Table 1: The classes of chemicals listed below will readily oxidize and ignite spontaneously in air.

Grignard reagents
Alkyl-lithium reagents
Various other metal alkyls and aryls
Various metal carbonyls
Alkali metals
Various metal powders
Various metal hydrides
Various nonmetal hydrides
Various nonmetal alkyls
Phosphorus (white/yellow)
Various gases

2. Reason for Policy

- a. Certain types of materials and their subsequent wastes must be handled by special procedures due to their highly hazardous nature. These chemicals can react violently/unpredictably during opening, routine handling or transport. The purpose of the policy and guidelines is to better manage unstable, highly hazardous materials or materials that can become unstable over time in order to reduce the risk associated with their handling. If injuries were to result from improper management or handling of these potentially unstable materials, then laboratories could also be cited by OSHA.

3. Responsibilities

- a. DO NOT purchase large quantities of pyrophoric materials. Purchase the amount that you will use in a 3-6 month time period.
- b. All materials should be stored in an inert atmosphere or medium when possible. For handling and use information please see EH&S procedures for Safe Use of Pyrophoric/Water-Reactive Reagents.
- c. Due to the potential instability of the materials, researchers need to contact Environmental Health & Safety for guidance and disposal of all pyrophoric chemicals and related materials
- d. Researchers should not use pyrophoric reagents until they have read and fully understood the guidelines; however, reading these guidelines does not substitute for hands-on training.

- e. New users of pyrophoric reagents must work under the close supervision of the PI or designated experienced user.
  - f. All experiments/procedures should be considered a two-person task and personnel should not work alone.
  - g. All labs working with pyrophoric materials must have in place written SOPs and documented training for each person working with these materials.
  - h. Proper PPE must be worn at all times and all emergency equipment must be in compliance.
  - i. All incidents involving pyrophoric materials (i.e. spills, exposures, fires, etc.) must be reported to PI and, when necessary, EH&S.
  - j. All waste/unwanted materials must be completely quenched or stabilized by the addition of compatible solvent before it can be removed by EH&S. Additional charges incurred for handling expired/unstable materials through our waste vendor will be charged back to the appropriate department or lab.
4. Sanctions
- a. All penalties and fines are the responsibility of the university department in which the infraction occurred. Grant funding may not be used to pay regulatory fines or penalties.

## Procedures:

### Protocol for Safe Use of Pyrophoric and Water-Reactive Reagents

#### 1. Overview

- a. Pyrophoric and water-reactive materials can ignite spontaneously on contact with air, moisture in the air, oxygen, or water and therefore must not be exposed to the atmosphere. Specific examples of materials are given below. Failure to follow proper handling procedures outlined by the college can result in fire or explosion, leading to serious injuries, death, and/or significant damage to facilities. Any handling of a pyrophoric/water-reactive material is high risk and must be controlled with adequate system design, direct supervision and training.
- b. Researchers should not use these reagents until they have read and fully understood these guidelines; however, reading these guidelines does not substitute for hands-on training. New users of pyrophoric/water-reactive reagents must work under the close supervision of the PI or designated experienced user. All experiments/procedures should be considered a two-person task and personnel should not work alone. All labs working with these materials must have in place written standard operating procedures (SOPs) and documented training for each person required to handle these materials. Excellent definitions and technical guidance can be found in Aldrich Technical Bulletins AL- 134, AL-164, AL-195, and AL-211. (<https://www.sigmaaldrich.com/chemistry/chemical-synthesis/learning-center/technical-bulletins.html>)

#### 2. Explanations of Pyrophoric Materials

- a. OSHA 1910.1200 and NFPA 45 both define a pyrophoric material as a liquid, solid, or gas that will ignite spontaneously in air at a temperature of 130 degrees F (54.4 degrees C) or below.
- b. 49 CFR 173.124(b)(1) defines a pyrophoric material as a liquid or solid that, even in small quantities and without an external ignition source, can ignite within five (5) minutes after coming in contact with air when tested according to UN Manual of Tests and Criteria.
- c. A variety of liquid, solid, and gas reagents are pyrophoric, including (but not necessarily limited to):
  - i. Grignard Reagents: RMgX (R=alkyl or aryl, X=halogen)
  - ii. Lithium alkyls and aryls: e.g. tert-butyllithium and n-butyllithium
  - iii. Other main group organometallics and certain transition metal organometallics: e.g. trimethylaluminum and diethylzinc
  - iv. Metal carbonyls: e.g. nickel tetracarbonyl
  - v. Alkylmetal alkoxides or halides (dimethylaluminum chloride, diethylethoxyaluminum)
  - vi. Metal hydrides (e.g. potassium hydride, sodium hydride, lithium aluminum hydride)
  - vii. Low molecular weight alkyl phosphines and arsines: e.g. tributyl phosphine and trimethyl arsine
  - viii. White phosphorus
  - ix. Alkali metals in zerovalent form (lithium, sodium, potassium, especially sodium potassium alloy – NaK, and even more dangerous are cesium and rubidium)
  - x. Metal Powders (finely divided): e.g. cobalt, iron, zinc, zirconium, magnesium
  - xi. Finely divided sulfides and phosphides, such as iron sulfides (FeS, FeS<sub>2</sub>, Fe<sub>3</sub>S<sub>4</sub>), potassium sulfide (K<sub>2</sub>S), aluminum phosphide (AIP)
  - xii. Used hydrogenation catalysts (Raney-Ni is especially hazardous due to adsorbed hydrogen)
  - xiii. Copper fuel-cell catalysts (e.g. Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>)
  - xiv. Boranes, including monomeric or diborane, and certain of its lower alkyl derivatives (R<sub>3</sub>B)
  - xv. Silane (SiH<sub>4</sub>) and some silane derivatives

#### 3. Hazards

- a. Whenever possible, pyrophorics/water-reactive materials should be handled under inert atmospheres or in such a way that rigorously excludes air/moisture since they can ignite upon contact with air and/or water. They all tend to be toxic and many come dissolved in a flammable solvent. Other common hazards include corrosivity, teratogenicity, water reactivity, peroxide formation, along with damage to the liver, kidneys, and central nervous system. Personnel should always consult the SDS, manufacturer and EH&S for technical advice before they begin work with these materials.
- b. Pyrophoric Gases

- i. There are several kinds of pyrophoric gases that should be included in any discussion of pyrophoricity. Many of these are used in manufacturing microelectronics and nanomaterials development. The example gases presented here have four things in common: 1) they ignite readily upon exposure to air, 2) they are all nonmetallic hydrides, 3) Many chemical derivatives of these compounds are also pyrophoric and 4) they are all highly toxic inhalation hazards. Always consult with EH&S prior to the start of a project involving the use of highly toxic or pyrophoric gases.
  - ii. Arsine (AsH<sub>3</sub>) - (also known as arsenic hydride) is a colorless, highly toxic gas that is heavier than air and has a distinctive garlic-like odor. Acute exposure to the material produces rapid intravascular hemolysis (destruction of red blood cells) and hemoglobinuria (hemoglobin in urine), while chronic exposure can result in anemia; peripheral neuropathy; numbness, tingling, and weakness of the extremities; and cardiovascular disease. In general, arsine will not ignite in air unless at elevated temperatures, but it can be detonated by a suitable heat source, shock wave, or electrostatic discharge. Arsine may also exist in other compounds and the ignition temperature of many arsine containing compounds can be lower than that of arsine. All arsine compounds should be considered pyrophoric until they are properly characterized.
  - iii. Diborane (B<sub>2</sub>H<sub>6</sub>) - is a highly toxic, colorless gas with a repulsive but sweet odor; it is highly reactive and flammable. Depending on the concentration and duration, inhalation exposure to diborane can produce symptoms ranging from central nervous system depression and fatigue/drowsiness to pulmonary edema and pulmonary hemorrhage. Diborane forms flammable mixtures with air over a wide range (flammable limits, 0.9% and 98%) and its ignition temperature can range between 38 °C and 52 °C (100 °F and 125 °F); spontaneous ignition can take place at standard temperature, pressure and humidity. It reacts spontaneously with chlorine and forms hydrides with aluminum and lithium, which may ignite spontaneously in air. It reacts with many oxidized surfaces as a strong reducing agent, and reacts violently with vaporizing liquid-type extinguishing agents. Diborane is most often purchased and used in the monomeric form, borane, where it exists as a complex with solvent or another electron donor. Hydrolysis in water generates copious amounts of hydrogen that can rapidly build up pressure in a closed vessel.
  - iv. Phosphine (PH<sub>3</sub>) - is a highly toxic colorless gas with an ignition temperature of 212 °F, often igniting spontaneously. In addition, at elevated temperatures, phosphine decomposes, emitting highly toxic fumes of PO, which react vigorously with oxidizing materials. It possesses the characteristic putrefying odor of a mixture of garlic and decaying fish. Prolonged exposure to very low concentrations will cause chronic poisoning, characterized by anemia, bronchitis, gastro-intestinal disturbances, and visual, speech, and motor difficulties.
  - v. Silane (SiH<sub>4</sub>) - also known as silicon tetrahydride, is a colorless gas with a choking effect (putrid odor). It can ignite in air, especially in the presence of other hydrides as impurities. However, 99.95% pure silane ignites in air unless emerging at very high gas velocities, whereas mixtures of up to 10% silane may not ignite. Hydrogen liberated from its reaction with air (atmospheric oxygen) often ignites explosively. Silanes react violently with chlorine and bromine. When silane reacts with a moist medium, such as the lungs, it can form silicic acid (further reacts with oxygen to form silicon dioxide) which can lead to silicosis of the lungs. All silanes should be considered pyrophoric until they are properly characterized. Halon should not be used as an extinguishing agent on silane fires.
- c. Pyrophoric Solids (metals and nonmetals)
- i. There are numerous solids that are pyrophoric and in general, they can be divided into two classes: 1) metals and 2) non-metals
  - ii. Nonmetals: There are several allotropes of phosphorus (P). The two most common are white (or yellow) phosphorus and red phosphorous. Red phosphorus is not classically considered pyrophoric; however, red phosphorus ignites easily and produces phosphine (a pyrophoric gas) during combustion. Additionally, when red phosphorus is heated to >260 °C, it can change allotropes to white phosphorus. Pyrophoric (white or yellow) phosphorus is a colorless to yellow, translucent, waxy solid. It ignites spontaneously on contact with air at or above 30 °C (86 °F). Phosphorus is explosive when mixed with oxidizing agents. Fumes from burning phosphorus are highly irritating but only slightly toxic except in very high concentrations. Like red phosphorus, white phosphorus also produces phosphine during combustion. Phosphorus fires should be drenched with water until the fire is extinguished and then covered with wet sand. Alternatively, a dry chemical fire extinguisher can be used. The solidified phosphorus should then be covered with wet sand, clay, or ground limestone.
  - iii. Metals (including alkali group I & II metals): Nearly all metals will burn in air under certain conditions. Some are oxidized rapidly in the presence of air or moisture, generating sufficient heat to reach their ignition temperatures. Others oxidize so slowly that heat generated during oxidation is dissipated before the metal becomes hot enough to ignite. Certain metals, notably magnesium, titanium, sodium, potassium, NaK alloys, lithium, zirconium, hafnium, calcium, plutonium, uranium, and thorium, are referred to as combustible metals because of the ease of ignition when they reach a high specific area ratio (thin sections, fine particles, or molten states). However, the same metals in massive solid form are comparatively difficult to ignite.
  - iv. Properties of burning metal fires can cover a wide range, such as the following: 1) Burning titanium produces little smoke, while burning lithium smoke is dense and profuse. 2) Some water-moistened finely divided metals, such as zirconium, burn with near explosive violence, while the same powder wet with oil burns quiescently. 3) Sodium melts and flows while burning; calcium does not. 4) Some metals (e.g., uranium) have a tendency to burn long after exposure to moist air, while prolonged exposure to dry air makes it more difficult to ignite. 5) Some metals (especially heavy metals) can be toxic or fatal if they enter the bloodstream or their smoke fumes are inhaled. 6) A few metals, such as thorium, uranium, and plutonium, emit ionizing radiation that can complicate fire fighting and introduce a radioactive contamination problem. Where possible, radioactive materials should not be processed or stored with other pyrophoric materials because of the likelihood of widespread radioactive contamination during a fire.

v. Since fires involving combustible metals can require techniques/materials not commonly encountered in conventional fire-fighting operations, it is necessary for those responsible for controlling combustible metal fires to be thoroughly trained prior to an actual fire emergency. Metal fires should never be approached without proper protective equipment (clothing and respirators). Always review MSDSs to understand the properties of pyrophoric solids, conditions in which they become pyrophoric, storage and handling practices, processing hazards, and methods of extinguishing fires involving these kinds of metals. Metal fires are best extinguished with sand or the use of a metal fire-rated fire extinguisher.

d. Pyrophoric Liquids

i. Many of the organometallics and organometal/organometalloid hydrides listed above can come as neat reagents or dissolved in a highly flammable solvent, for example THF, hexane, diethyl ether, etc., which creates several other hazards to consider, such as splashing/spraying, skin absorption (toxicity), inhalation hazards, and fire. The number of known and potential pyrophoric liquids is too long to list; however an example list of some commonly used organolithium compounds is shown below. Please see links below and the manufacturer's MSDS for guidance/information regarding the specific material that is being used.

ii. Examples of Alkyls

- i. Methylolithium lithium bromide complex solution
- ii. Methylolithium solution in diethoxymethane, diethyl ether, or cumene/THF
- iii. Ethyllithium solution in benzene/cyclohexane (9:1)
- iv. Isopropyllithium solution in pentane
- v. Butyllithium solution in hexanes, heptanes, pentane, toluene, or cyclohexane
- vi. Isobutyllithium solution in heptane
- vii. sec-Butyllithium solution in cyclohexane
- viii. tert-Butyllithium solution in heptanes or pentane
- ix. (Trimethylsilyl)methylolithium solution in pentane
- x. Hexyllithium solution in hexane
- xi. 2-(Ethylhexyl)lithium solution 30-35 wt. % in heptane

iii. Examples of Alkynyls

- i. Lithium acetylide, ethylenediamine complex 90%
- ii. Lithium acetylide, ethylenediamine complex 25 wt. % slurry in toluene
- iii. Lithium (trimethylsilyl)acetylide solution in tetrahydrofuran
- iv. Lithium phenylacetylide solution in tetrahydrofuran

iv. Examples of Aryls

- i. Phenyllithium solution in di-n-butyl ether

v. Other Examples

- i. 2-Thienyllithium solution in tetrahydrofuran
- ii. Lithium tetramethylcyclopentadienide
- iii. Lithium pentamethylcyclopentadienide

4. Controlling the Hazards

a. Pyrophoric and water-reactive reagents (liquids or solids) are easily manipulated under the inert atmosphere of an efficient glove box. Therefore, it is highly recommended that reagents (liquids or solids) be used whenever possible within the confines of the glove box or equivalent. Caution must be exercised with contaminated glassware, wipes, spatulas, gloves, or septa from the glove box. When possible, the contaminated equipment should be neutralized inside the glove box prior to removal. However, if this cannot be accomplished, the equipment should be brought out of the glove box in a container under an inert atmosphere, connected to an inert gas line, and neutralized as appropriate. If an inert atmosphere glove box is not available and a pyrophoric reagent, such as t-butyllithium solution, needs to be used, the solution can be transferred by either a syringe or double-tipped needle (cannula) outside the glove box only if the transfer takes place under an inert atmosphere using proper handling techniques. The potential hazards/reactivity for each material must be reviewed and the appropriate safety measures taken prior to the start of the experiment.

b. BEFORE working with pyrophoric/water-sensitive reagents, users must complete the following:

- i. Consult with your PI to receive approval before working with highly hazardous materials.
- ii. Read the relevant Material Safety Data Sheets (MSDS), technical bulletins, and guidance documents to aid in the recognition and reduction of potential hazards. The MSDS must be reviewed before using an unfamiliar chemical and periodically as a reminder.
- iii. Perform a hazard analysis and identify the potential failures or weak points in your experimental design. Be prepared to handle accidents.
- iv. Prepare a written Standard Operating Procedure (SOP) identifying the safety precautions specific to the operations. All training must be documented in writing.
  - i. Perform a "dry run" to identify and resolve possible hazards before conducting the actual procedure.
  - ii. Identify method of transfer based on volume of material used (syringe vs. cannula)
  - iii. Users of pyrophoric materials must be trained in proper lab technique and be able to demonstrate proficiency.
  - iv. Search for alternative materials/techniques in your experiment in order to minimize risk and the amount of hazardous waste generated.
- v. All work must be conducted in a fume hood or glove box.
- vi. Know the location of eyewash/shower, fire extinguishers, fire alarm pulls, and emergency exits.
- vii. Do not work alone or off hours when there are few people around to help.
- viii. Wear the appropriate personal protective equipment.

- i. Use a lab coat, goggles/face shield and gloves.
    - ix. Maintain good work practices.
      - i. Keep combustible materials, including paper towels, wood, and plastics, away from pyrophoric/water-reactive reagents.
      - ii. Minimize the quantity of reagents used and stored
      - iii. All syringe transfers must be performed with a needle-lock Luer syringe
      - iv. Use the smallest quantity of material practical. It is better to do multiple transfers of small volumes rather than attempting to handle larger quantities. However, when transferring volumes that are >50mL or that exceed 50% of the syringe, an alternate method should be employed (e.g. use a larger syringe or perform a cannula transfer). If cannula transfers are necessary to perform, be extremely cautious not to over pressurize the container. A standard pressure range for a transfer with inert gas on a vented apparatus is between 3-5 psi.
      - v. In order to reduce the possibility of clogging during transfer of materials, use a larger bore needle, such as a 16-18 gauge needle. Remove all excess and nonessential chemicals and equipment from the fume hood or glove box where pyrophoric chemicals will be used to minimize the risk of fire.
    - x. NEVER return excess chemical to the original container. Small amounts of impurities introduced into the container may cause a fire or explosion.
    - xi. All recurring minor procedural incidents, including small flash fires, must be evaluated and managed in order to avoid any potential for major incidents. All corrective actions should be discussed with PI (in some cases, EH&S) and documented.
  - c. Personal Protective Equipment
    - i. Chemical splash goggles or safety glasses that meet the ANSI Z.87.1 1989 standard must be worn whenever handling pyrophoric chemicals. Ordinary prescription eyeglasses will NOT provide adequate protection unless they also meet this standard. When there is the potential for splashes, goggles must be worn, and when appropriate, a face shield added.
    - ii. A face shield, worn over safety eyewear, is required any time there is a risk of explosion, large splash hazard or a highly exothermic reaction.
    - iii. All manipulations of pyrophoric chemicals which pose this risk must take place in a fume hood with the sash in the lowest feasible position.
    - iv. In general, disposable-type chemical protective gloves do not provide a robust barrier to skin contact when working with pyrophoric materials. If the reactive material were to ignite and spill onto the hand, nitrile or latex gloves could also ignite and contribute to serious injury. Additionally, latex or nitrile gloves offer little to no protection against exposure to certain carrier solvents, such as tetrahydrofuran. Overall, it is critical to consider the physical hazard, as well as the chemical hazard when working with pyrophoric materials. Nomex® and related aramid fiber products are excellent fire retardant materials, but can significantly reduce dexterity. For optimal protection and dexterity, it is recommended that fire-retardant gloves, such as a Nomex® flight glove be worn over a glove that provides adequate protection against chemical exposures.
    - v. A flame-resistant laboratory coat or coveralls should be worn when using pyrophoric reagents. Flame -resistant materials such as flame-retardant treated cotton and Nomex® provide thermal protection. They can ignite but will not continue to burn after the ignition source is removed. Flame-resistant clothing should meet the American Society for Testing and Materials standard, ASTM F2302: Standard Performance Specification for Labeling Protective Clothing as Heat and Flame Resistant.
    - vi. Synthetic clothing (made from synthetic polymers) is strongly discouraged, because it is often highly flammable.
    - vii. Appropriate shoes that cover the entire foot (closed toe, closed heel, no holes in the top) must be worn at all times. For optimal protection, we strongly recommend the use of leather shoes.
  - d. Safety Equipment
    - i. Fire Extinguishers
      - i. The recommended fire extinguisher is a standard combustible metals (D) type. DO NOT use a carbon dioxide, Halon, or water-based fire extinguisher to extinguish a pyrophoric material fire as these types of extinguishers can exacerbate the fire in certain scenarios. In addition to the appropriate fire extinguisher, a container of dry sand or soda ash (lime) should be kept in the work area to extinguish any small fire that occurs, such as at the syringe tip and to receive any last drops of reagent from the syringe and also as a general absorbent. All fire extinguishers in the laboratory and common rooms must be checked monthly by laboratory personnel or a departmental designee and class D (combustible metals) signs must be present to indicate the location of this fire extinguisher type.
      - ii. If you are in need of a class D fire extinguisher for your lab space, please contact EH&S at 314-446-8133.
    - ii. Glove Box or Glove Bags
      - i. Glove boxes are excellent devices to control pyrophoric chemicals when inert or dry atmospheres are required. Routine preventative maintenance should be performed to ensure the glove box maintains the proper atmospheric conditions (i.e. check for leaks, rips/tears, dry rot, etc.). Alternatively, glove bags are relatively cheap devices that will allow for the safe weighing/transfer of pyrophoric materials in a protected environment. However, they should be used inside a fume hood and they should undergo rigorous leak testing before each experiment.
    - iii. Gas Cabinets
      - i. Gas cabinets, with appropriate remote sensors and fire-suppression equipment, are required.

- ii. 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 in order to prevent backflow. Please contact your gas supplier for assistance.
  - iii. Emergency back-up power should be provided for all electrical controls, alarms and safeguards associated with the pyrophoric gas storage and process systems.
  - iv. Please review the UHSP Fume Hood and Eyewash/Emergency Shower policies.
5. Storage and Disposal
- a. Storage
    - i. Pyrophoric/water-reactive materials must be stored in accordance with International Building Code 2009 and local fire district requirements. Please contact EH&S for additional storage considerations. In general:
      - i. When possible, store pyrophoric chemicals in a rated flammables storage cabinet away from other flammable materials. Always plan ahead to minimize the available flammable material (i.e. solvents) in the immediate vicinity.
      - ii. When refrigeration of materials is required, materials must be stored in an approved explosion-proof refrigerator/freezer.
      - iii. Store as recommended in the MSDS. A nitrogen-filled desiccator or glove box is considered to be suitable storage locations for these materials.
      - iv. If pyrophoric reagents are received in specially designed shipping, storage or dispensing containers, (such as the Aldrich Sure/Seal packaging system) ensure that the integrity of that container is maintained.
      - v. Ensure that sufficient protective solvent, oil, kerosene, or inert gas remains in the container while the material is stored.
      - vi. DO NOT return excess chemical to the original container. Small amounts of impurities introduced into the container may cause a fire or explosion.
      - vii. During storage, it is possible for sufficient solvent to evaporate that highly active pyrophoric material crystallizes from solution (e.g. lithium aluminum hydride in THF). It should be recognized that these situations call for particular caution if the cap should be removed.
      - viii. For storage of excess chemical, prepare a storage vessel in the following manner:
        - i. Select a septum that fits snugly into the neck of the vessel
        - ii. Dry any new empty containers thoroughly
        - 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 vent the flask and quickly inject inert gas through a second needle to maintain a blanket of dry inert gas above the reactive reagent.
        - v. Once the vessel is fully purged with inert gas, remove the vent needle, then the gas line.
      - ix. For long-term storage, the septum should be secured with a copper wire (Figure 1A).
      - x. For extra protection a second same-sized septa can be placed over the first (Figure 1b).
      - xi. The additional use of parafilm can help to maintain the integrity of the materials during storage.
      - xii. **See "Figure 1A: Septum wired to vessel" and "Figure 1B: Second septa for storage" at bottom.**
  - b. Disposal of Pyrophoric Materials
    - i. A container with any residue of pyrophoric materials should never be left open to the atmosphere.
    - ii. 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.
    - iii. The empty container should be rinsed three times with a 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.
    - iv. The empty, quenched container can be placed in the broken glass container, while the solvent rinses and water rinse should be disposed as hazardous waste and should not be mixed with incompatible waste streams.
    - v. All consumable materials that are contaminated with pyrophoric chemicals should be quenched and disposed of as hazardous waste.
    - vi. If the lab is disposing of older, potentially dried out materials through EH&S rather than neutralizing, the containers must be partially refilled with the original inert carrier material so that the dried material is adequately covered (e.g. dried out LiAlH<sub>4</sub> needing additional THF or Lithium metal ribbons needing additional mineral oil).
    - vii. Alert EH&S for any wastes contaminated by pyrophoric/water-reactive chemicals by adding in comments during the electronic submission process.
    - viii. All waste-related material should be stored appropriately (e.g. kept in the fume hood or flammables cabinet) until it is removed by EH&S.
    - ix. EH&S cannot remove materials from the lab until they have been appropriately stabilized/quenched and deemed safe for transport.
6. Emergency Spill/Accident Procedures
- a. Shut off all ignition sources and allow spilled materials to react with atmospheric moisture.
  - b. A container of powdered lime or sand should be kept within arm's length when working with a pyrophoric material and it should be used to completely smother and cover any spill that occurs.
  - c. DO NOT use water to attempt to extinguish a pyrophoric material fire as it can actually enhance the combustion of some pyrophoric materials (e.g. metal compounds).
  - d. Do not use combustible materials (paper towels) to clean up a spill, as these may increase the risk of igniting the pyrophoric compound.

- e. Know the location and function of all appropriate emergency equipment.
  - f. If anyone is exposed, or on fire, wash body with copious amounts of water and try to remove contaminated clothing.
  - g. Depending on your location, report all spills/fires by calling 314-446-7233.
  - h. Recurring incidents should be evaluated for process improvement and hazard mitigation.
7. Conclusion
- a. Pyrophoric/water-reactive reagents can be handled and stored safely as long as exposure to atmospheric oxygen and moisture is limited appropriately. All work with pyrophoric/highly-toxic gases must be reviewed by EH&S prior to start. Some finely divided solids must be transferred under an inert atmosphere in a glove box or glove bag, or under an inert-gas funnel. Liquids may be safely transferred without the use of a glove box by employing techniques and equipment discussed in the Aldrich Technical Information Bulletin AL-134. Always wear appropriate PPE. Always maintain a clutter-free work area to reduce the risk of spills and potential fires. NEVER engage in experiments that require the use of pyrophoric materials without the proper documented training.

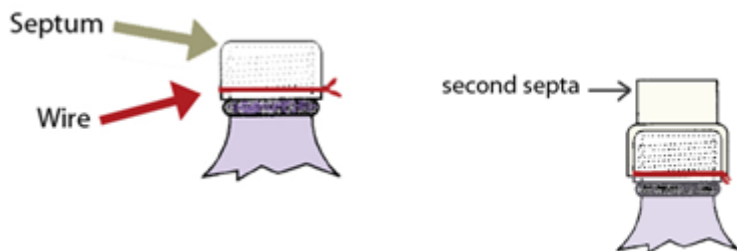


Figure 1A: Septum wired to vessel Figure 1B: Second septa for storage

**Resources:**

- UHSP PPE Policy
- UHSP Fume Hood policy
- UHSP Emergency Eyewash and Shower policy

**Policy Contacts:**

<u>Name</u>	<u>Contact Information</u>
Eric Knoll	311-446-8375
Carlin Harp	314-446-8133