Managing Pyrophoric and Water Reactive Chemicals in the Laboratory

National Institutes of Health (NIH) • Office of Research Services (ORS) • Division of Safety (DS)

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Safe Use of Pyrophoric and Water Reactive Chemicals in the Laboratories

Pyrophoric materials are liquids or solids that can ignite instantaneously without an external ignition source when in contact with air/moisture. Extreme care must be taken while handling these chemicals to avoid fire/explosion leading to serious injuries to personnel and damage to the facility.

Below are some examples of pyrophoric and water reactive materials commonly found in research laboratories:

- Organolithium reagents (e.g., alkyl and aryl lithiums, lithium acetylide, lithium amide)
- Organohalogen or Grignard reagents (e.g., RMgX, where R=alkyl and X=halogen)
- Alkyl metal bases (e.g., butyllithiums, trimethylaluminum, triethylboron)
- Metal hydrides (e.g., sodium hydride, lithium aluminum hydride, sodium borohydride)
- Finely divided metals (e.g., Raney nickel, aluminum powder, zinc dust)
- Metal carbonyls (e.g., nickel carbonyl, iron pentacarbonyl)
- Aluminum alkyls (e.g., trimethylaluminum)

Hazards

The primary hazard of pyrophoric/water reactive materials is the ignition of the material when exposed to air or moisture. Other hazards may include corrosivity, peroxide formation, and toxicity.

For chemical specific hazard information, refer to manufacturers' labels and safety data sheets (SDS).

Purchase and Storage

- Minimize the purchase of the pyrophoric/water reactive materials to quantities just enough for the application or enough to meet the needs of a few months.
- Store these materials in accordance with SDS recommendations, away from sources of heat/ignition, , flammable and combustible materials and other incompatible chemicals(Chemical Segregation Table). Store in airtight secondary containment to reduce the potential for exposure to air and moisture.
- Pyrophoric liquids are generally packaged in glass bottles under an inert atmosphere and sealed with a septum to prevent air intrusion. Never expose these liquids to air/moisture.
- Store pyrophoric solids under an inert atmosphere or under mineral oil as per SDS.
- Containers carrying pyrophoric materials must be clearly labeled with the correct chemical name and hazard warning. Date all containers upon receipt and opening.
- Periodically check the condition of the container and the material. Some of the chemicals like potassium metal can form peroxides and superoxides over time even under mineral oils.
- Pyrophoric and water reactive chemicals stored in glove boxes must be sealed when not in use.

Working Safely with Pyrophoric and Water Reactive Materials

General Precautions

Quantities of the pyrophoric reagents used in any process/experiment shall be limited to the minimum required amount, and procedures and SOPs shall be developed by the researcher in advance of the usage to control fires/vigorous reactions. A container of powdered lime or a bucket of dry sand should be kept within arm's length while working with pyrophoric/water reactive chemicals. Use powdered lime/sand to completely smother and cover any spill and call for

emergency help. Never use paper towels or other combustive materials to clean spills. Additional controls may be required based on the hazards of the specific chemical used, amount used, type of application etc. Consult with your Safety Specialist for guidance.

Engineering Controls

Pyrophoric/water reactive materials ideally should be handled inside a glovebox under an inert atmosphere. When this is not possible, handle inside a properly functioning chemical fume hood by following special techniques described later in this document to prevent exposure to air/oxygen/water. Keep the sash of the fume hood at the lowest feasible position.

Personal Protective Equipment (PPE)

Eye Protection

Safety goggles or safety glasses with side shields that meet the ANSI Z.87.1 1989 standard must be worn while handling pyrophoric/water reactive chemicals. General prescription glasses are not appropriate for providing adequate protection. Additional protection like a face shield may be required if the risk of explosion, splash or a highly exothermic reaction exists.

Hand Protection

Appropriate gloves must be worn when working with pyrophoric/water reactive chemicals. Nitrile gloves are appropriate for handling small quantities and refer to SDS for chemical specific recommendations. Consider the use of fire-resistant (FR) gloves or liners if needed.

Lab Coat

Flame resistant or NOMEX lab coats are required when working with pyrophoric/water reactive chemicals. Clothing made of natural fibers must be worn under the lab coat and on legs. Clothing made of synthetic fibers such as polyester and nylon tend to melt to the body when exposed to flames while clothing made of natural fibers such as cotton tend to char.

Access to Safety Equipment

Eyewash and Safety Shower

Access to plumbed emergency eyewash stations and safety showers within 10 seconds, or 55 feet of unimpeded access from the hazard, are required.

Fire Extinguisher

Access to a Class D fire extinguisher within 10 seconds, or 55 feet of unimpeded access is required if the laboratory is working with a considerable amount of pyrophoric material or finely divided metal powder.

Laboratory workers must be trained in the location and use of all the emergency equipment present in the lab. Keep the emergency phone numbers clearly posted and readily accessible.

Laboratory Specific Standard Operating Procedure (SOP)

Laboratories using and storing pyrophoric/water reactive chemicals must develop a lab specific SOP covering procurement, storage, use, emergency response and disposal. PI/supervisor is responsible for developing the SOP and all laboratory personnel should be made familiar with and review the completed SOP. Contact your DS Safety Specialist for guidance.

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Training

Pyrophoric materials should be handled only by trained/experienced personnel. Users must be trained by the PI/supervisor on:

- How to handle pyrophoric reagents including storage, emergency response, waste management, neutralization/quenching of the excess reagent/rinsate etc.
- Review of SDSs and the lab specific SOP.
- Laboratory policies on working alone and prior approvals
- Any additional lab specific training/approval processes etc.
- Lab Safety training provided by DS

To provide approval to work with pyrophoric/water reactive reagents the PI/supervisor must verify the competency of the employee to perform the tasks safely and respond to emergencies. The training must be documented, and the records must be maintained by the PI/Supervisor.

Handling Pyrophoric Liquids

Before starting work, all people working with or around pyrophoric materials must read the manufacturer's SDSs, lab specific SOPs and other available reference materials.

Never allow any combustible materials, including paper products, to come in contact with pyrophoric/water reactive chemicals. Remove all unnecessary items including equipment and chemicals from the fume hood. Syringes, needles, and glassware must be completely dry and purged with an inert gas prior to use with pyrophoric/water reactive chemicals.

Everything used for the transfer (needles, syringes etc.), the experimental assembly and any other equipment that encountered pyrophoric liquids must be rinsed with a neutral solvent and the rinsate must be quenched following the "quenching guidelines" at the end of this document.

Using Syringe to Transfer Pyrophoric Liquid

- Secure pyrophoric reagent bottle to a stand with a clamp prior to starting the transfer to prevent it from tipping. Syringing out the liquid with one hand holding the bottle while the other managing the syringe is not an acceptable practice.
- Always use long needles that (18 gauge or higher) to reach the liquid and never try tilting the reagent bottle.
- Always use a syringe that has at a minimum double the capacity of the volume being transferred.
- Never use syringes for the transfer of more than 10ml of a pyrophoric liquid. Double-Tipped Needle (Cannula) must be used for transfer of quantities exceeding 10ml.

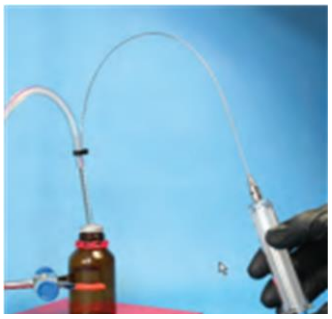

Fig 1. Filling syringe using inert gas pressure. Image from Aldrich Technical Bulletin AL-134

Fig 2. Syringe transfer of reagent to reaction flask. Image from Aldrich Technical Bulletin AL-134

To syringe out pyrophoric liquids from the bottle first insert a needle that is attached to an inert gas line through the septum to the headspace above the reagent without touching the liquid. Insert a long needle (18 gauge or higher) that is firmly attached to a syringe to the reagent bottle through the septum. Pressure of the inert gas will slowly push the plunger back when the reagent starts to fill in the syringe. Once the required amount is inside the syringe, pull the needle out of the liquid and by gently pushing the plunger send any excess reagent along with any air bubbles back into the reagent bottle. Extreme caution must be taken to prevent the plunger getting separated from the syringe. Quickly transfer the reagent to the reaction flask (Fig. 2) through the septum by carefully pushing the plunger.

Using a Double-Tipped Needle (Cannula) to Transfer Pyrophoric Liquid

Double-tipped needle (cannula) method should be used when transferring liquids more than 10ml. Insert one end of the double -tipped needle through the septum to the reaction flask/dropping funnel and the other end of the needle to the reagent through the septum of the bottle. Insert another needle attached to an inert gas line (<1 psi) into the reagent bottle through the septum into the headspace without touching the liquid. The reagent will start flowing to the reaction flask/dropping funnel when the tip of the double -tipped needle lowered to the liquid inside the reagent bottle. Pull the end of the double -tipped needle out of the reagent slowly once you have completed the transfer of the required volume. The reaction flask must be vented throughout the process and kept under an inert atmosphere to prevent air from entering the system.

Refer to Aldrich Technical Bulletins AL-134 and AL-164 for detailed instructions on how to safely transfer liquids using syringe and double tipped needle (cannula).

Pyrophoric reagents should be added slowly to the reaction flask while cooling in a cooling bath (e.g., acetone/dry ice etc.) to control the reaction rate. The syringe, needle and the double tipped needle used for transfer must be rinsed with a non-reacting solvent at the end of the transfer and the rinsate must be neutralized/quenched carefully.

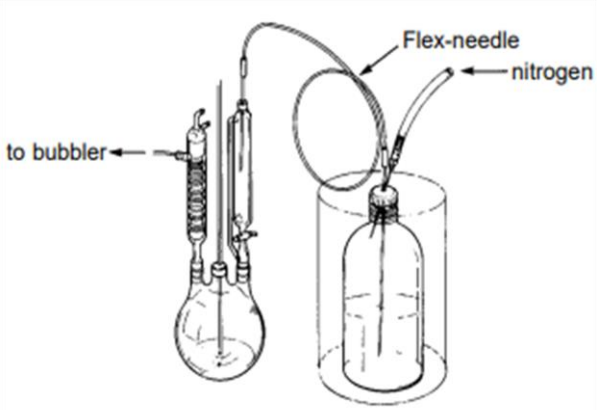

Fig 3. Double-tipped needle transfer of pyrophoric liquids. Image from Aldrich Technical Bulletin AL-164

Handling Pyrophoric/Water Reactive Solids

Even though pyrophoric solids are slightly more stable in the air than pyrophoric liquids, all precautions described for liquid pyrophorics (PPE, SOP, Engineering controls, access to emergency equipment etc.) must be followed while handling pyrophoric solids.

Because of the reactivity, most of the pyrophoric/water reactive solids are sold either as mineral oil dispersions or completely submerged in hydrocarbon solvents. The safest approach for handling these solids is performing all manipulations under an inert atmosphere inside a glove box.

Weighing and Transferring Pyrophoric/Water Reactive Solids

Before opening the reagent bottle for weighing/transferring, ensure that all the required equipment/supplies are ready to avoid prolonged exposure of the pyrophorics to air.

To weigh metals like sodium and potassium, the first step is to cut the required amount using a dry knife while the metal is coated with hydrocarbon/ mineral oil. Transfer the cut metal immediately to a flask with toluene/hexane to wash out the oil. To weigh out the final amount, transfer the washed material to a pre-weighed flask containing toluene/hexane. Once the final amount is weighed out, carefully transfer to the reaction flask. All handling and transfer of the metal must be done using a dry tweezer or a similar device. Never use low boiling solvents like pentane for washing to avoid water condensation.

Metal hydrides of sodium and lithium are generally sold as oil dispersions and may be handled in the air for brief periods of time. Weighing these oil dispersions must be done carefully under a fume hood, using a pre-weighed flask with a septum and sealed under an inert gas. Remove the mineral oil by repeating washings using dry hexane injected through the septum. The washings syringed out from the flask must be carefully quenched by using isopropanol. Never add solvent to dry metal hydrides, always add metal hydrides slowly to the anhydrous solvent in the reaction flask. Seal the reagent bottle after flushing with an inert gas before storage.

Do not cut pieces of pyrophoric metals like sodium on paper towels or other combustible materials and do not clean up residues or small spills of pyrophoric materials using paper towels. Contaminated paper products can ignite and can cause fire/explosion. Never leave containers with pyrophoric/water reactive chemicals and residues open to expose the materials to air/moisture to prevent fire/explosions.

Pyrophoric solids that are discolored or have any unusual appearances should never be used. These materials may be unstable. When these conditions are found, never touch/move the container and contact your Safety Specialist and DEP (301-496-7990) immediately. Some of the pyrophoric solids like potassium and sodium are peroxide formers.

Quenching of Pyrophoric Liquids and Solids

Quenching of excess reagents and the cleaning of used glassware can be very dangerous and should be done very carefully. Dissolve or disperse excess pyrophoric reagents (liquids and solids) in an inert solvent like toluene before quenching. Everything used in an experiment involving pyrophoric materials (syringe, a double-tipped needle (cannula), spatula, glassware assembly, etc.) must be rinsed with an inert solvent and the rinsate must be transferred to a flask under an inert atmosphere for quenching. Cool the rinsate/solvent containing pyrophoric material using a cooling bath (e.g., acetone/dry ice) before starting the quenching process. Slowly add isopropyl alcohol to the cooled toluene suspension to initiate the quenching process. Continue the addition of isopropanol until no further heat/bubbles are released. Methanol is then added slowly followed by copious amounts of water to ensure no active pyrophoric material is left in the solution. Continue stirring for another hour and slowly bring the solution to the room temperature. When all signs of reaction (i.e. bubble and/or heat production) cease, dispose the solution as hazardous waste by following NIH Waste Disposal Guide.

There are some instances where transferring or washing out all the pyrophoric/water reactive materials from the contaminated items can be very difficult, for example, alkali metals stuck to a spatula. They may be quenched by carefully adding ice if the amount is extremely small. It is very important to add the material to a large quantity of ice while stirring to control any exothermic reaction. No organic solvent should be added during this process to avoid the potential for flammable materials catching fire. Continue stirring the ice mixture and slowly warm up to the room temperature. Once all signs of reaction have completely ceased, dispose the mixture as hazardous waste.

Emergency Response

Spills involving pyrophoric materials are very dangerous due to the potential for spontaneous combustion. Any spill involving pyrophoric materials is considered as a large spill. **Follow NIH Chemical Spill Response Procedures** . Cover

the spill with powdered lime or dry sand if safe to do so before contacting emergency services. Never use paper towels or other combustive materials to clean or cover pyrophoric/water reactive material spills.

If anyone is exposed, or on fire, wash under a safety shower and get medical attention immediately by following the guideline below.

Emergency medical help and spills:	Contact Emergency Services/Fire Department. **Bethesda, MD -** call 911 on-campus, 9-911 off-campus**;** 301-496-9911 (cell phone) **Baltimore, MD -** 911 **Frederick, MD -** 911 **Hamilton, MT -** 911 **Research Triangle Park, NC -** 911 (landline), 919-541-2800 (cell phone)

The injury/exposure should be immediately reported to your supervisor and local OMS clinic as described below.

For eye & dermal exposure, wash immediately under eyewash or safety shower for at least 15 minutes.	Seek **emergency medical help** if needed as described above. The injury/exposure should be immediately reported to your supervisor and local OMS clinic: **Bethesda, MD**: Building 10, Room 6C306; (301) 496-4411 **Baltimore, MD**: 251 Bayview Blvd., BRC 01B210; (667) 312-5843 **Frederick, MD:** 8200 Research Plaza, Room 1B116; (301) 631-7233 **Hamilton, MT:** 903 South 4th Street, Room 5202; (406) 375-9755 **Research Triangle Park, NC:** 111 T W Alexander Drive, Building 101, Room E111; (984) 287-4178

Waste Disposal

Follow the NIH Waste Disposal Guide for disposal of pyrophoric/water reactive materials and any contaminated items including the quenched materials.

References

1. Aldrich Technical Bulletins AL-134 and AL-164
2. Methods for the safe storage; handling; and disposal of pyrophoric liquids and solids in the laboratory