Chemical Class Standard Operating Procedures

Aluminum Alkyl and Halide Compounds
Settlement Classes: Pyrophorics and Water Reactives

Department:	Chemistry
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Location:	Whitaker Hall Room 243

Section 1: Process, Hazardous Chemical, or Hazardous Class

Chemical(s)	Use(s)
Aluminum alkyl Compounds	1. Quenching of pyrophoric liquids, such as aluminum alkyls, left after reactions
Liquid pyrophoric chemicals	2. Transferring of liquid pyrophoric chemicals

Section 2: Definition of Chemical group and Properties

Pyrophoric materials can ignite spontaneously on contact with air, moisture in the air, oxygen, water, or other chemicals with reactive hydroxyl groups. Most pyrophorics may also be classified as water reactives. However, not all water reactives are pyrophoric. The reaction rates of pyrophorics with air is in the order of $Rate_{SOLID} < Rate_{LIQUID} \leq Rate_{GAS}$. Many pyrophorics are supplied as solutions in flammable solvents such as hexane. The hazards of the mixture, pyrophoric and the solvent, should be considered together and procedures for safe handling should reflect the hazard properties of both solvent and solute. If you have questions concerning the applicability of any recommendation or requirement listed in this procedure, contact the Principal Investigator of your Laboratory (Dr. Greg Boyce).

Section 3: Potential Hazards

Pyrophoric materials are defined as chemicals that spontaneously (within 5 minutes) ignite on contact with air or moisture. Because these reagents react on contact with air and/or water, they must be handled under an inert atmosphere and in such a way that rigorously excludes air/moisture. Many come dissolved or immersed in a flammable solvent that may be hazardous. Besides extreme flammability, most of these materials are toxic and may cause damage to the liver, kidneys, and central nervous system.

Controlling the Hazards

- BEFORE working with pyrophoric or water reactive reagents, read the relevant SOP, Material Safety Data Sheets (MSDS), technical bulletins, and guidance documents to understand how to mitigate the hazards. The MSDS must be reviewed before using an

unfamiliar chemical and periodically as a reminder. Users of reactive materials must be trained in proper lab technique and be able to demonstrate proficiency.

- Do not work alone or during off hours, when there are few people around to help. The first few times you handle pyrophoric materials, seek more experienced researchers to show you proper technique and always let others in the lab know you will be working with pyrophoric materials. ALWAYS wear proper personal protective equipment.
- Remove all excess and nonessential chemicals and equipment from the fume hood or glove box where pyrophoric or water reactive chemicals will be used. This will minimize the fuel if a fire should occur. Keep combustible materials, including paper towels and Kimwipes, away from reactive reagents.
- Minimize the storage of pyrophoric or water reactive materials in your lab by ordering the smallest practical amount; handle and use the smallest practical quantity. It is safer to do multiple transfers of small volumes than to attempt to handle larger quantities at once. Alternatively, an appropriately engineered system, capable of safely transferring the larger quantity must be designed, tested and properly used.

Section 4: Personal Protective Equipment

Use what is listed below unless other lab-specific information is included in the Protocol/Procedure section.

Eye and Face Protection

ANSI-approved safety glasses with side shields or chemical splash goggles must be worn at all times when handling chemicals in the lab.

Skin and Body Protection

1. Gloves are required when handling hazardous chemicals.
    a. Specific glove type recommendations are provided in the Protocol/Procedure section.
    b. Inspect gloves prior to use. Use proper glove removal technique (without touching glove's outer surface) to avoid skin contact with this product. Wash and dry hands after handling chemicals, before breaks, and at the end of the workday.
2. Lab coats are required when handling hazardous chemicals in the lab.
    a. Nomex 3A flame-resistant lab coats are required when working with pyrophorics (H250) and explosives (H200, H201, H202, H203)
    b. Flame resistant lab coats (Nomex or other material) should be worn when working with hazardous chemicals as a Category 1 or 2 flammable liquids (H224 and H225).
3. Cotton-based, non-synthetic clothing (including long pants; no skin exposed below the waist) should be worn.
4. Closed-toe and closed-heel shoes are required in the lab.

Section 5: Engineering Controls

The following is the set of engineering controls required when handling pyrophorics materials:

- Work under an inert atmosphere (e.g., argon, nitrogen) in a glove box, vacuum manifold or any enclosed inert environment inside a fume hood.
- Keep the material under inert atmosphere (e.g., nitrogen, argon) when not in use.

- Only when absolutely nexessary to transfer larger quantities of pyrophorics, use an appropriately designed, engineered system that is tested and properly used.
- Before removing pyrophoic materials from the glovebox, review the proper steps necessary to protect the material from air, or quench material before exposing it to air.

Section 6: Special Handling and Storage Requirements

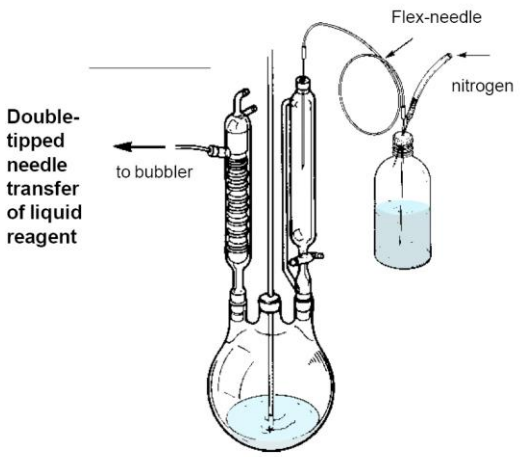
General Background for Pyrophoric Materials

- Pyrophorics spontaneously react and generally ignite in air. Pyrophoric solids generally smolder before igniting; pyrophoric liquids generally ignite immediately on exposure to air; pyrophoric gases may form jet fires if escaping from a vessel following a mechanical failure.
- Most pyrophorics react violently with water. Therefore, water should not be allowed to contact pyrophoric materials.
- Pyrophorics must be handled under an inert atmosphere that rigorously excludes air/moisture. Many pyrophorics are supplied dissolved or immersed in a flammable solvent that may pose additional hazards requiring stringent handling precautions.
- Most of these materials are toxic and may cause damage to the liver, kidneys, and central nervous system.
- Pyrophoric chemicals may also have other hazardous properties in addition to those described above. Safe use requires assessing all potential hazards.

Handling Pyrophoric Liquids

Users should read and understand the Aldrich Technical Information Bulletin, No. AL-134; there are many detailed handling recommendations that are not presented in this SOP.

- There are two basic techniques to transfer pyrophoric liquids: the syringe and the cannula needle. The syringe is normally preferred for small quantities (i.e. less than 20 mls0 as describe in NO AL-134: (http://www.signmaaldrich.com/etc/medialib/docs/Aldrich/Bulletin/al_techbull_al134.Par.0001.file.tmp/al_techbull_al34.pdf).
- These reagents can be handled safely in the laboratory, if proper syringe techniques are used. The reagent can be dispensed using a syringe or double-tipped needle (16, 18 or 20 gauge) inserted through the hole in the metal cap, as shown in the figure below. A Schlenk line in a fume hood with inert gas flow will be necessary. The Aldrich Sure/Seal™ Packaging System provides a convenient method for storing and dispensing air-sensitive reagents. It is recommended that the plastic cap be replaced after each use and, in particular, for long-term storage.



- Most researchers only need to use small quantities, so the syringe method works best. Be cautious with the use of the plastic syringe as the rubber gasket may swell up leaving you with a syringe of pyrophoric liquid. Start with small quantities, until you are proficient with the method.

Storage of Pyrophoric Materials

- Use and store minimal amounts of pyrophoric chemicals. Do not store reactive chemicals with flammable materials or in a flammable liquids storage cabinet. Containers carrying reactive materials must be clearly labeled with the correct chemical name and hazard warning in English.
- Store reactive materials as recommended in the MSDS or product guidance. Inert gas-filled desiccators or glove boxes are suitable storage locations for most materials. Refrigerated material should be stored in non-combustible containment, away from flammables.
- If pyrophoric or water reactive reagents are received in a specially designed shipping, storage or dispensing container (such as the Aldrich Sure/Seal packaging system) ensure that the integrity of that container is maintained.
- Ensure that a sufficient protective solvent, oil, kerosene, or inert gas remains in the container while the material is stored.
- NEVER return any excess chemical to the original container. Small amounts of impurities introduced into the container may cause a fire or explosion. Excess material can be used up as part of the experimental procedure or quenched using an appropriate technique.
- For storage of any excess chemical, prepare a storage vessel in the following manner:
    - Dry any new empty containers thoroughly (i.e.in an oven).
    - Insert the septum into the neck in a way that prevents atmosphere from entering the clean, dry (or reagent filled) flask.
    - 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.
    - Once the vessel is fully purged with inert gas, remove the vent needle then the gas line.

    To introduce the excess chemical, use the procedure described in the handling section, below.
- For long-term storage, the septum should be secured with a copper wire (figure 1A).
- For extra protection a second same-sized septa (sans holes) can be placed over the first (figure 1b).
- Use parafilm around the outer septa; remove the parafilm and outer septum before accessing the reagent through the primary septum.

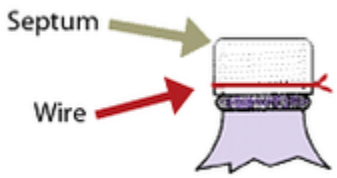


Fig. 1A Septum wired to vessel

Fig. 1B For long-term storage, use a second septum

Section 7: Spill and Accident Procedures

- DO NOT use water to attempt to extinguish a reactive material fire as it can enhance the combustion of some reactive materials, e.g. metal compounds.
- Do not use combustible materials (paper towels) to clean up a spill, as these may increase the risk of igniting the reactive compound. Soda ash (powdered lime) or dry sand should be used to completely smother and cover any small spill that occurs. Also for a very small spill (i.e. tip of the needle) you can let the material burn itself out in the fume hood.
- A container of Metal X, soda ash (powdered lime) or dry sand should be kept within arm's length when working with a reactive material.
- If anyone is exposed, or on fire, drench in the safety shower with copious amounts of water.
- In the case of a metal fire, smothering the fire is a better course of action than use of water.
- The recommended fire extinguisher is a standard dry powder (ABC) type. Class D extinguishers are recommended for combustible solid metal fires (e.g, sodium, LAH), but not for organolithium reagents. Contact the EH&S Fire Prevention team and/or review the MSDS for the appropriate fire extinguisher.
- Call 9-1-1 for emergency assistance and for assistance with all fires, even if extinguished.
- Pyrophoric gas releases and associated fires, should be extinguished by remotely stopping the gas flow. Never attempt to put out a pyrophoric gas fire if the gas is flowing. Further information on working with pyrophoric and toxic gases can be found here: http://ehs.berkeley.edu/images/ehs/pubs/32toxgas.pdf .

Section 8: Decontamination Procedures:

- All materials - disposable gloves, wipers, bench paper, etc. - that are contaminated with pyrophoric chemicals should be disposed of as hazardous waste. Proper and complete hazardous waste labeling of containers is important.
- The contaminated waste should be placed in a metal container away from other combustibles to prevent fires. Verify the material is no longer pyrophoric before placing waste in with other combustible waste.

Section 9: Waste Disposal Procedures:

- Any container with a residue of hazardous reactive materials should never be left open to the atmosphere.
- Any unused or unwanted air reactive materials must be destroyed by transferring the materials to an appropriate reaction flask for hydrolysis and/or neutralization with adequate cooling. If you have large quantities of unreacted pyrophoric reagent material contact EH&S for guidance on disposal options.
- The empty container should be rinsed three times with an inert dry COMPATIBLE solvent; this rinse solvent must also be neutralized or hydrolyzed. Neutralization should be done in cold bath to better control the neutralization. The rinse solvent must be added to and removed from the container under an inert atmosphere.

- After the empty container is triple-rinsed, it should be left open in back of a hood or ambient atmosphere at a safe location for about a week.
- The empty container, solvent rinses and water rinse should be disposed of as hazardous waste and should not be mixed with incompatible waste streams.

Section 10: Matrial Safety Data Sheet Loactions:
SDS can be accessed online at http://ucmsds.com