KENT STATE UNIVERSITY

Effective Date:

Standard Operating Procedure

SOP Title: Pyrophoric Safety & Standard Operating Procedures
Principal Contact:
Room and Building:
Lab Phone Number:

Purpose

The purpose of this standard operating procedure (SOP) is to ensure that pyrophoric materials are handled and disposed of properly using good laboratory practices (GLP). This SOP outlines anhydrous procedures for safety, handling, disposal, and emergencies involving pyrophoric materials. Pyrophoric materials ignite spontaneously when in contact with air by reacting with oxygen, air moisture, or both. Failure to follow proper protocols when handling pyrophorics can result in fire or explosion, leading to serious injuries/death or significant damage to facilities.

Examples of Pyrophoric Materials (not an all-inclusive list):

- ***Organolithium reagents*** - typically in hydrocarbon solvents. Note: *tert*-butyllithium solutions are highly pyrophoric.
- ***Organomagnesium reagents*** - including Grignard reagents (RMgX) - Typically in hydrocarbon solvents. Neat reagents are pyrophoric.
- ***Organoaluminum reagents*** - Neat or in hydrocarbon solvents. Neat reagents are highly pyrophoric.
- ***Organozinc reagents*** - Neat reagents are pyrophoric.
- ***Boranes*** - Neat reagents are pyrophoric; diborane
- ***Non-Metal Alkyls*** - R_3B, R_3P, R_3As; tetramethyl silane, tributyl phosphine
- ***Phosphorus***
- ***Potassium***
- ***Sodium***
- ***Gases*** - Silane, dichlorosilane, phosphine, arsine

User Responsibilities

All users are responsible for following the parameters outlined in this SOP when pyrophoric materials are being employed for experimentation. This SOP does not count as a complete SOP for use of pyrophoric materials. Users must include the procedures that they are using for their own experiments as well.

Training

All personnel who use pyrophoric materials must have successfully completed a training session from their supervisor on the safe operating procedures. Documentation of trained personnel is to be acknowledged at the end of this SOP.

Equipment for Pyrophoric Use

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.

Potential Hazards

Pyrophorics must be handled under inert atmospheres and in such a way that excludes air/moisture since they will ignite when exposed to 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, and toxicity.

Incomplete quenching of pyrophorics may also result in a fire (see "Quenching of Pyrophorics Standard Operating Procedure" for details). If isopropanol has been added to the flask, even a small amount of unquenched material may be capable of igniting this solvent. As a result, it is essential that the material be completely consumed during the quenching process.

Safety Precautions

BEFORE beginning work with pyrophoric materials, users must:

- Complete required EH&S Online Safety Training through Flashtrain.
- Consult with their PI (Principal Investigator) and receive approval when working with highly hazardous materials.
- Read the relevant Safety Data Sheets (SDS) to understand how to diminish hazards associated with using pyrophoric chemicals. The SDS must be reviewed before using an unfamiliar chemical and periodically as a reminder.
- Prepare a written Standard Operating Procedure identifying the safety precautions for specific operations, example on pg. 7).
    - Consider performing a "dry run" to identify and resolve possible hazards associated with the actual procedure.
- Know the location of eyewashes/safety showers, fire extinguishers, fire pull alarms, and emergency exits.
- Wear appropriate personal protective equipment, including a lab coat, goggles/face shield, and gloves.
- Maintain GLP:
    - Keep combustible materials, e.g., paper towels and Kim wipes, away from pyrophoric reagents.
    - Minimize the quantity of pyrophoric reagents used and stored and use the smallest quantity of material practical. 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.
  - Remove all excess and non-essential chemicals and equipment from the fume hood or glove box where pyrophoric chemicals will be used to minimize the risk of fire.
  - Designate a fume hood or glove box for hazardous work.

Storage Protocols

- Use and store minimal amounts of pyrophoric materials.
- Do NOT store pyrophoric chemicals with flammable materials or in a flammable cabinet.
- Pyrophorics are best stored in a nitrogen-filled desiccator or glove box.
- NEVER return excess chemical to the original container as small amounts of impurities introduced into the container could cause a fire or explosion.
- For storage of excess chemical, prepare a storage vessel in the following manner:
  - Select a septum that fits snugly into the neck of the vessel.
  - Dry any new empty containers thoroughly.
  - Insert septum into 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.
  - For long-term storage, the septum should be secured with a copper wire (figure 1A).
  - For extra protection a second same-sized septa (without holes) can be placed over the first (figure 1b).
  - Use parafilm around the outer septa and (obviously) remove the parafilm and outer septum before accessing the reagent through the primary septum[3].

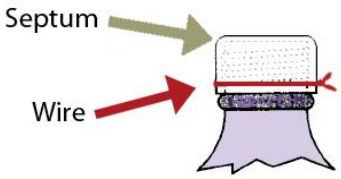

Fig. 1A Septum wired to vessel

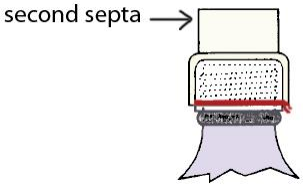

Fig. 1B For long-term storage, use a second septum

Incident Response

- Fires resulting from pyrophoric ignition may be smothered with sand or extinguished with a powder or sand fire extinguisher.
- <u>DO NOT</u> use a CO_2 fire extinguisher or water to attempt to extinguish a pyrophoric material fire as these can enhance combustion of some pyrophoric materials. 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.
- If anyone is exposed, or on fire, wash body with copious amounts 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.
- Call 911 for emergency assistance
- Any fires resulting from pyrophoric materials MUST be reported to the Chemical Health & Safety Coordinator and your supervisor.

Spill Response

Spill – Small

- Exert extreme caution due to potential spontaneous combustion.
- Call for a coworker to provide backup.
- Place a fire extinguisher nearby.
- Powdered lime (calcium oxide, CaO) or dry sand should be used to completely smother and cover any spill that occurs.
- Carefully quench by slow addition of isopropanol.
- After complete quench, double bag spill residues for hazardous waste pickup.

Spill - Large

- Exert extreme caution due to potential spontaneous combustion.
- Call 911 for emergency assistance.
- Evacuate the spill area.
- Post someone or mark-off the hazardous area with tape and warning signs to keep other people from entering.
- Provide emergency personnel with technical advice on the chemicals involved.

Disposal

Pyrophoric Reagents

- A container with any residue of pyrophoric materials should NEVER be left open to the atmosphere.
- Any unused or unwanted pyrophoric materials must be destroyed by quenching.
- The essentially empty container should be rinsed three times with an inert dry 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.
- After the container is triple-rinsed, it should be left open in back of a hood or ambient atmosphere at a safe location for at least a week. After the week, the container should then be triple rinsed again.
- The empty container, solvent rinses and water rinse should be disposed as hazardous waste.
- See “Quenching of Pyrophorics Standard Operating Procedure” for more details.

Pyrophoric Contaminated Materials

- All materials that are contaminated with pyrophoric chemicals should be disposed as hazardous waste. Proper and complete hazardous waste labeling of containers is vital.
- Alert EH&S for any wastes contaminated by pyrophoric chemicals.
- The contaminated waste should not be left overnight in the open laboratory but must be properly contained to prevent fires.

Methods for Transferring of Pyrophoric Chemicals

Method 1: Syringe

- In a fume hood or glove box, clamp the reagent bottle to prevent it from moving.
- Clamp/secure the receiving vessel too.
- After flushing the syringe with inert gas, depress the plunger and insert the syringe into the Sure/Seal bottle with the tip of the needle below the level of the liquid
- Insert a needle from an inert gas source carefully keeping the tip of the needle above the level of the liquid
- Gently open the inert gas flow control valve to slowly add nitrogen gas into the Sure/Seal bottle.

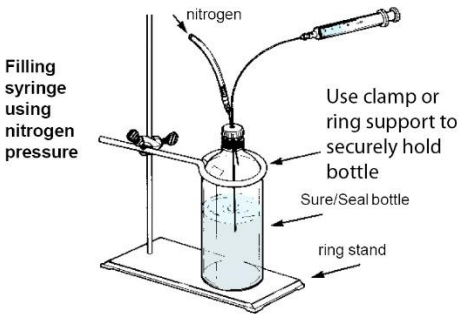

Fig. 2A Filling syringe using nitrogen pressure

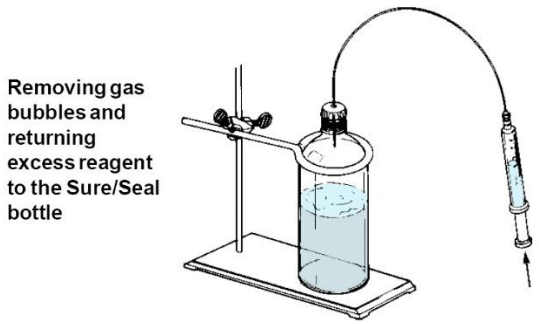

Fig. 2B Removing gas bubbles and returning excess reagent to the Sure/Seal bottle

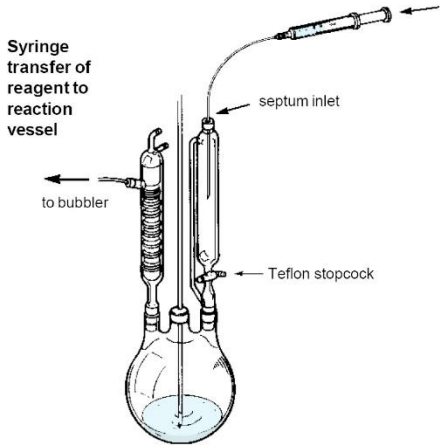

Fig. 2C Syringe transfer of reagent to reaction vessel

- This will allow the liquid to slowly fill the syringe (up to 100mL) as shown in **Fig. 2A**. Pulling the plunger causes gas bubbles.
- Let nitrogen pressure push the plunger to reduce bubbles. Excess reagent and entrained bubbles are then forced back into the reagent bottle as shown in **Fig. 2B**.
- The desired volume of reagent in the syringe is quickly transferred to the reaction apparatus by puncturing a rubber septum as illustrated in **Fig. 2C**.

Method 2: Cannula (i.e., Double-Tipped Needle)

- The double-tipped needle technique is recommended when transferring 50 mL or more.
- Pressurize the Sure/Seal bottle with nitrogen and then insert the double-tipped needle through the septum into the headspace above the reagent. Nitrogen will pass through the needle. Insert the other end through the septum at the calibrated addition funnel on the reaction apparatus. Push the needle into the liquid in the Sure/Seal reagent bottle and transfer the desired volume. Then withdraw the needle to above the liquid level. Allow nitrogen to flush the needle. Remove the needle first from the reaction apparatus and then from the reagent bottle. **(Fig. 3A)**

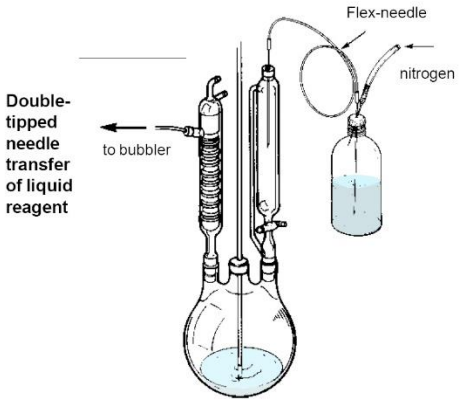

Fig. 3A Double-tipped needle transfer of liquid reagent

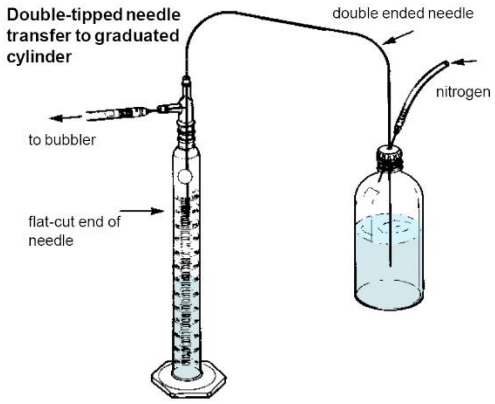

Fig. 3B Double-tipped needle transfer to graduated cylinder

- To control flow rate, fit a Luer lock syringe valve between two long needles as shown in **(Fig. 3C)**.

- For an exact measured transfer, convey from the Sure/Seal bottle to a dry nitrogen flushed graduated cylinder fitted with a double-inlet adapter **(Fig. 3B)**. Transfer the desired quantity and then remove the needle from the Sure/Seal bottle and insert it through the septum on the reaction apparatus. Apply nitrogen pressure as before and the measured quantity of reagent is added to the reaction flask.

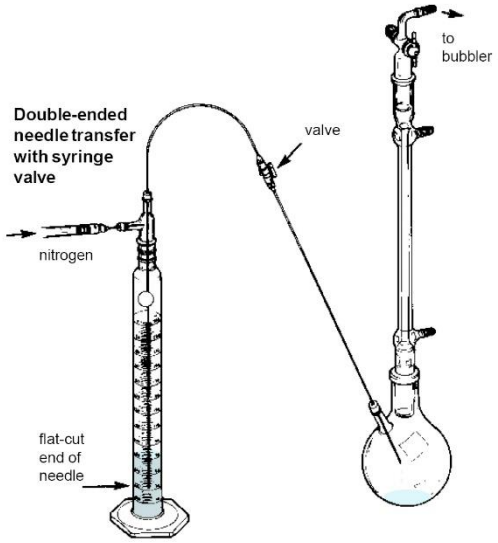

Fig. 3C Double-ended needle transfer with syringe valve

Lab Specific Use Procedures

The following minimum requirements must be met when defining lab specific use procedures:

- Identify designated use areas within the laboratory for highly hazardous chemicals
- Include:
    - 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 considered to present high risk by lab personnel.

An example of what lab-specific tasks may look like are provided below:

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.

Add as many tasks as necessary.

References

Procedures for Safe Use of Pyrophoric Reagents. (May 10, 2009). UCI EH&S. https://www.chemistry.ucla.edu/sites/default/files/safety/sop/SOP_Pyrophoric_Liquid_Reagents.pdf.

Effective Date:

Pyrophoric SOP Training

Name	Lab Group	Date	Signature