Administrative Information

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| --- | --- | --- | --- |
| School |  | Department |  |
| PI name |  | PI email |  |
| Lab manager name (if applicable) |  | Lab manager email (if applicable) |  |
| Locations covered by this SOP (buildings/rooms) |  | | |
| SOP version number |  | SOP approval date |  |
| Reviewed and approved by (name) |  | Reviewed and approved by (initials) |  |
| **Emergency contact name** |  | **Emergency contact phone\*** |  |
| Secondary emergency contact name |  | Secondary emergency contact phone\* |  |
| \* Provide emergency contact phone numbers that will be active both during normal work hours and after hours, e.g., personal mobile phone. Alternatively, give separate daytime and after-hours numbers for both contacts. | | | |

SOP Requirements

Instructions document You are responsible for reading the [SOP Instructions](https://tiny.cc/usc-sop-instructions) outlining roles, responsibilities, and other important safety information. In addition, you must include that document as part of your records.

Recordkeeping Acknowledgement forms for this SOP and any associated training are included at the end of this document. Additional copies of the forms are available online ([SOP Acknowledgement](https://tiny.cc/usc-sop-acknowledgement), [Internal Training Record](https://tiny.cc/usc-sop-training)).

Customization It is intended that personnel add lab-specific information to the SOP template to produce a finished and functional SOP. Sections that require additional information and customization are highlighted in yellow throughout the document.

Standard (Safe) Operating Procedure: *Pyrophoric Liquids*, *Pyrophoric Solids*, and Category 1 *Chemicals Which, in Contact With Water, Emit Flammable Gases*

Scope: Pyrophoric gases This SOP does NOT cover pyrophoric gases. In general, pyrophoric gases should be stored and handled using equipment professionally designed and engineered for that purpose, incorporating appropriate safety features which at a minimum shall meet regulatory requirements (LA Fire Code, etc). Typically, safety features will include flame detectors, automatic gas shut-off, leak detectors, exhausted gas cabinets, etc. Pyrophoric gas systems should be covered by a system-specific SOP which should be based on the manufacturer’s operating manual.

Scope: Liquids and solids This SOP provides general safety guidance for the safe storage and use of pyrophoric liquids and solids and the related Category 1 *chemicals which, in contact with water, emit flammable gases*. It does not by itself provide detailed instructions on air-sensitive chemistry techniques.

Hazard and classification Cal/OSHA (and OSHA) define hazard classes *Pyrophoric Liquid* and *Pyrophoric Solid*; each has only one subdivision, that being Category 1. For both hazard classes, the basic definition is the same, that being a material which “*…even in small quantities, is liable to ignite within five minutes after coming into contact with air.*” ([§1910.1200 Appendix B](https://www.osha.gov/laws-regs/regulations/standardnumber/1910/1910.1200AppB))

OSHA defines two other hazard classes which are related to pyrophorics, these being *Self-Heating Chemicals* and *Chemicals Which, in Contact With Water, Emit Flammable Gases*.

Self-heating chemicals are capable of reacting spontaneously with air, with the production of heat, but unlike pyrophorics, they do not react with sufficient vigor to spontaneously ignite in small quantities, or within five minutes.[[1]](#footnote-1) However, storage under extreme conditions may result in thermal runaway leading to ignition, typically after hours to days. Extreme conditions in this context may include one or more of the following: Large amounts (kilograms) of material, external heat sources, thermal insulation, storage in unsealed containers. Self-heating chemicals are a significant hazard and risk when stored on an industrial scale, but the risk is relatively easy to mitigate on a laboratory scale.

Self-heating chemicals are subdivided into Categories 1 and 2, where Cat. 1 represents the highest hazard. Typical Cat. 1 self-heating chemicals are sodium dithionite (sodium hydrosulfite in obsolete nomenclature) and anhydrous sodium sulfide.

Unless used in an abnormal manner (e.g. on a giant scale) or unless the hazard is raised (e.g. by comminuting the material to form a high surface area powder), Category 1 self-heating chemicals do not require handling with the same precautions as pyrophorics and do not fall under the scope of this SOP.

[OSHA hazard communication regulations](https://www.osha.gov/laws-regs/regulations/standardnumber/1910/1910.1200AppB) state: “*Chemicals which, in contact with water, emit flammable gases are solid or liquid chemicals which, by interaction with water, are liable to become spontaneously flammable or to give off flammable gases in dangerous quantities.*”

*Chemicals which, in contact with water, emit flammable gases* are subdivided into three categories. Category 1 materials react vigorously with water at ambient temperature to produce a rapid stream of flammable gases. Additionally, if the gases have any tendency to spontaneously ignite, either because the reaction produces a lot of heat or because the gas is pyrophoric, then the material is classified as Category 1 regardless of the rate of gas evolution. Category 2 and Category 3 materials show decreasingly rapid evolution of flammable gases when in contact with water.

Category 1 *chemicals which, in contact with water, emit flammable gases* vary significantly in their tendency to ignite when exposed to air or moisture. The most reactive of these materials, for example alkali metals (Li, Na, K, etc)[[2]](#footnote-2) and many hydridic metal hydrides (e.g. NaH, CaH2, LiAlH4) are likely to ignite in contact with water or many other fluids, and may heat up and potentially ignite in contact with air, paper towels, and other carriers of moisture. Certain other Cat. 1 substances have a low probability of spontaneous ignition from water or air, common examples being sodium borohydride and sodium cyanoborohydride. Those Category 1 *chemicals which, in contact with water, emit flammable gases* which pose a significant hazard of spontaneous ignition should be stored and handled in the same manner as pyrophorics and this SOP shall apply. (See under *Hazard identification*, below, for how to distinguish between more and less hazardous Cat. 1 materials.)

Note that even the lower reactivity Category 1 *chemicals which, in contact with water, emit flammable gases* are still very reactive substances and may be a serious fire hazard (including spontaneous ignition) if mishandled, mixed with incompatible materials (e.g. acids, oxidizers), made more reactive by grinding to a high-surface-area powder, or if exposed to air or moisture under conditions which may result in thermal runaway (e.g. when in large quantities, or when external heat sources are present).

Additionally, thermal runaway is also a possibility when these materials are used under ill-conceived reaction conditions.

Please refer to Section 6 of the [CHP](http://tiny.cc/chem-hygiene-plan) for a detailed explanation of the GHS hazard classification system instituted by OSHA. **All personnel who agree to abide by this SOP are required to familiarize themselves with the contents of Section 6 of the CHP.**

Hazard identification For purchased chemicals, identification as *pyrophoric liquid*, *pyrophoric solid*, or *Category 1* *chemical which, in contact with water, emits flammable gases* should be made based on hazard information given in the safety data sheet (SDS). Furthermore, SDSs should be studied to determine if any additional hazards are present, for example, health hazards.

The [*Encyclopedia of Reagents for Organic Synthesis*](https://onlinelibrary.wiley.com/doi/book/10.1002/047084289X) (“e-EROS”) provides brief but useful information on handling, storage, and safety precautions for large number of common and uncommon chemicals. For example, the article on [sodium hydride](https://doi.org/10.1002/047084289X.rs073.pub2) explains how the dispersion in oil can be handled in air but the dry powder decomposes, heats up, and may spontaneously ignite in moist air. Furthermore, NaH in oil dispersion or as dry powder reacts violently with water, usually with ignition.

For the convenience of users, EH&S maintains [this spreadsheet](https://docs.google.com/spreadsheets/d/1MIFY9FzlHeO-4td4BGALFexB4iFEkp0YKMk_8KgCknc/edit?usp=sharing) of the more common pyrophorics and Category 1 *chemicals which, in contact with water, emit flammable gases*. For the latter materials, the spreadsheet identifies those which possess a significant ignition risk and which should therefore be handled as a pyrophoric. If there is any question about the reactivity and hazard of a specific Category 1 *chemical which, in contact with water, emits flammable gases*, please either handle it as a pyrophoric or email [labsafety@usc.edu](mailto:labsafety@usc.edu) for guidance (and to have it added to the spreadsheet).

Synthesis of pyrophorics and *chemicals which, in contact with water, emit flammable gases* shall only be done by suitably experienced researchers who have the necessary chemical knowledge to predict and understand the likely hazards of the compounds they may produce.

Nomenclature The term “water reactive” is ambiguous and is not an OSHA phrase, since many water reactive materials (e.g. titanium tetrachloride, phosphorus pentoxide, anhydrous aluminum chloride), while they react vigorously and potentially dangerously with water, do not produce flammable gases or fire, and are therefore not categorized as *chemicals which, in contact with water, emit flammable gases*. However, the latter phrase is cumbersome, so henceforth in this document, the term “Category 1 water reactive” will be employed instead, or the word “pyrophoric” will be used as a blanket descriptor covering both pyrophorics and the more hazardous members of the hazard class *chemicals which, in contact with water, emit flammable gases*.

Pyrophoric hazards in research The ability to self-ignite in air makes pyrophorics one of the most hazardous classes of chemical for laboratory use, especially in synthetic chemistry where pyrophorics are commonly used as reagents inside fragile glass apparatus, and pyrophoric liquids are frequently manipulated with syringes and cannulae.

Pyrophoric liquids are quite common in semiconductor research and manufacturing, where they are used as sources for chemical vapor deposition (CVD and MOCVD) and atomic layer deposition (ALD). They are also used for doping of semiconductors. These applications (especially ALD, where only small quantities of pyrophoric liquids are used) pose a significantly smaller risk than use of pyrophorics in chemical synthesis. This is because for the semiconductor applications, the pyrophoric materials are usually sealed inside robust stainless steel vessels (“bubblers”) which are bolted into the deposition machine before the valves are opened, and the possibility of spillage or unexpected reaction is very small (provided the manufacturer’s operating instructions are followed). The main hazard is often when the bubblers are changed out, but this is infrequent as usage rates are normally small, and again, risk should be low if the operating manual is followed.

The reactivity of pyrophorics towards air can be affected by certain factors, e.g. humidity or surface area. For example, coarsely crystalline lithium aluminum hydride may be stable on short exposure to low-humidity air but heat up sufficiently to ignite in damp air, whereas finely powdered material may become pyrophoric regardless of humidity. The quantity of material also has an effect, since some pyrophorics initially oxidize slowly and need to achieve thermal runaway to ignite. Thus, a few drops of a medium molecular mass trialkylphosphine (e.g. tributylphosphine) on a benchtop will at worst smoke slightly for a short time, but larger quantity spilled on tissue paper may ignite, due both to the large amount, and also due to the bigger area exposed to the air.

*n*-Butyllithium solution is another example of a pyrophoric which is most likely to just smoke slightly when a few drops are spilled. However, *n*-butyllithium solution is highly air-reactive (much more so than, for example, tributylphosphine) and a spill of a few mL on a benchtop, or a smaller spill on paper or clothing, is likely to ignite. *tert*‑Butyllithium solution, diethylzinc, and triethylaluminum are examples of pyrophoric liquids of the highest degree of hazard, which ignite essentially instantly when exposed to the air in any quantity, no matter how small.

All of the above factors should be taken into consideration when working with pyrophorics, to determine their associated hazards and the precautions required.

Hands-on training Due to the magnitude of the hazard posed by pyrophoric materials, especially liquids, it is essential all new users receive hands-on training from the PI (or suitably-experienced designee).

New users should be directly supervised when handling pyrophorics until the PI (or suitably-experienced designee) is satisfied with their competence.

Internal training records should be maintained.

Undergrads and minors Minors shall NOT be permitted to work with pyrophoric materials.

PIs shall give careful consideration on a case-by-case basis as to the suitability of pyrophoric work by an undergraduate placed in their research lab, considering the experience and competence of the student and the details of the proposed experiments. If work with pyrophorics is permitted by the PI, the undergraduate shall be under direct supervision by a suitably experienced lab member at all times during the procedure. Higher-hazard pyrophoric procedures shall not be done by undergraduates. Examples of higher-hazard procedures are those which:

* Use large volumes of liquid pyrophorics, OR
* Use any amount of “instant-igniting” pyrophorics such as *tert*-butyllithium or diethylzinc, OR
* Have potential for reactive hazards or thermal runaway.

Pyrophoric materials are generally not suitable for use in undergraduate teaching labs, except in cases where the procedure is done as a demonstration by an experienced TA, staff member, or professor (e.g. demonstration of alkali metals reacting with water).

Working alone Pyrophoric materials shall not be used by persons working alone. It is incumbent upon pyrophorics users to coordinate with colleagues to ensure at least one additional person is within or adjacent to the lab while pyrophorics are in active use. The additional person or persons providing coverage should have a general familiarity with pyrophorics hazards, emergency procedures, and this SOP.

At least two persons should be physically present within the lab during highest-hazard pyrophorics work (e.g. use of “instant-igniting” pyrophorics such as *tert*-butyllithium, diethylzinc, or trialkylaluminums).

Note that routine operation of an ALD (atomic layer deposition) machine is acceptable alone as there is essentially zero possibility of the operator contacting pyrophoric material. However, certain non-routine operations, notably changing out the bubbler, are riskier and should not be conducted alone.

[Add lab-specific rules here.]

Working hours Pyrophorics use shall take place within normal business hours whenever possible. The PI or suitably experienced designee (e.g. lab manager) should be aware in advance of out-of-hours pyrophorics work.

[Add lab-specific rules here.]

Specific substances [Add details of specific substances you will be using in the lab under this SOP.]

Designated work areas/signage Pyrophorics should only be used in a clearly designated area which may include the entire lab or specific sublocations. It is advisable to restrict pyrophorics use to fume hoods and inert atmosphere glove boxes. Fume hoods contain spills and may help prevent fire spread in the event of an incident. Inert atmosphere glove boxes eliminate the possibility of ignition (provided the glove box is functioning correctly). The designated work area should be signed “Warning — Pyrophoric” (or equivalent wording).

Pyrophoric work areas shall be free of extraneous flammable and combustible materials. Work areas should be organized and free of clutter.

Non-combustible secondary containment such as metal spill trays should be used for pyrophorics work whenever there is potential for spillage.

To prevent exposure of personnel, appropriate engineering safety controls (most commonly a fume hood) shall be used for all work which has potential to release health-hazardous vapor or particulates (dust, powder, spray, or liquid/solid aerosol). Please consult the [CHP](http://tiny.cc/chem-hygiene-plan) for detailed information on engineering safety controls.

[Add lab-specific information here.]

Emergency equipment Appropriate fire extinguishants shall be available within the work area. For liquid pyrophorics dissolved in organic solvents (e.g. butyllithium) a normal Class ABC extinguisher is appropriate, though it is recommended to also have dry sand available. For combustible metals and metal hydrides, a Class D loose extinguishant (e.g. dry sand) with applicator or a Class D extinguisher shall be available.[[3]](#footnote-3)

A Class ABC extinguisher is unlikely to work for alkylaluminums, which require a Class D extinguishant.

Loose solid extinguishants such as dry sand shall have a suitable method of applying the extinguishant provided. This can be some kind of shovel or scoop with an appropriately long handle. Alternatively, the extinguishant can be stored in a long (e.g. 4-5 ft) tube open (or loosely capped) at one end, so the extinguishant can be poured onto a fire from a safe distance (see adjacent image for an example). Extinguishants shall be stored in an accessible position and clearly labeled. Ideally, containers of Class D extinguishant should be painted yellow (as shown in the adjacent image). Sufficient extinguishant (at least several kg) should be provided, since significant amounts are needed to completely cover even a small fire.

It is highly recommended to have a jug of dry sand available within arm’s reach whenever liquid or solid pyrophorics are used, so small spills can be immediately covered, preferably before they ignite. This shall be in addition to and not a replacement for the appropriate extinguisher options discussed above. (A jug of sand to hand may assist with rapidly tacking a small spill or minor fire, but it cannot replace the need for a proper extinguisher or larger quantity of Class D extinguishant in the event of a larger spill or fire.)

A safety shower and eyewash shall be easily accessible from all locations where pyrophoric materials are stored or used.

Unattended experiments Due to the vagaries of academic research, an absolutist approach to unattended experiments is not viable. The PI should develop appropriate rules for their lab, based on the guidelines below, and document them in this SOP.

Highest-hazard experiments involving pyrophorics (e.g. chemical synthesis using liquid pyrophorics) shall as far as possible not be left unattended (and never unattended for more than a few minutes) until all the pyrophoric material has been consumed or neutralized.

Experiments of intermediate hazard and risk using pyrophorics such as potassium, sodium, and metal hydrides shall as far as possible not be left unattended. However, some experiments of this kind are very slow, so unattended operation may be unavoidable on occasion.

Lower-hazard pyrophoric experiments (e.g. chemical vapor deposition using professionally designed and constructed equipment with automated operation and engineered safety features) may be left unattended at the PI’s discretion.

No experiments using pyrophorics shall be left unattended if there is a potential reactive hazard, e.g. thermal runaway.

Items contaminated with residual pyrophoric shall be quenched and cleaned in a safe manner before the worker leaves the area.

Items may include cannulae and syringes used with liquid pyrophorics, and blades, tweezers, and cutting boards used to cut and handle alkali metals.

Unattended hazardous experiments should be signed according to the requirements of the [Unattended Experiments Fact Sheet](https://tiny.cc/usc-unattended-operations). Due to the hazard of pyrophorics, the PI (or suitably experienced designee) should be aware of and approve all unattended experiments.

[Add lab-specific rules on unattended pyrophorics experiments.]

Inventory control Inventories of pyrophoric materials should be tightly controlled and the minimum quantities purchased and stored consistent with the work to be done. As a general rule, don’t stockpile more than a six month supply of pyrophoric materials without adequate reason. For example, having more than a six month supply of expensive pyrophoric liquid in a bubbler for chemical vapor deposition is entirely reasonable, whereas an active organic synthesis lab having a year’s supply of butyllithium on-hand is likely to be excessive.

The lab’s online chemical inventory shall be updated whenever pyrophoric materials are purchased or disposed.

Potassium metal and potassium alloys are time-sensitive due to potential formation of an explosive crust. (Metallic rubidium and cesium may do the same, but are extremely uncommon.) They shall be stored in accordance with the requirements of the [CHP](http://tiny.cc/chem-hygiene-plan) and the [EH&S time sensitive chemical webpage](https://ehs.usc.edu/research/lab/time-sensitive-chemicals/other-time-sensitive-chemicals); in particular, the time limits and inspection requirements shall be adhered to.

Finish one container before opening the next. Avoid accumulating multiple partly-used containers of the same pyrophoric material. The PI should ensure staff have checked the online and physical inventory before approving orders for pyrophorics.

Consider disposing of pyrophorics which are not required for active or probable upcoming laboratory work.

Segregation and storage Pyrophorics in storage shall be kept separate from oxidizers, acids, and other incompatible materials. With few exceptions (e.g. alkylphosphines, white phosphorus), pyrophorics are incompatible with aqueous solutions and shall be segregated from them. Many pyrophorics are incompatible with halogenated organics, for example, alkali metals may ignite or explode on contact with chlorinated solvents.

Pyrophorics in storage shall be kept separate from flammables and combustibles to the greatest possible extent. For example, pyrophorics should not be stored in a flammable cabinet full of organic solvents. If significant quantities of pyrophorics are stored then a dedicated flammable cabinet and/or dedicated flammable-rated refrigerator or freezer are recommended.

However, given the space constraints on labs, it is understood there are occasions when, for example, pyrophorics have to be stored in the same refrigerator as flammable materials.

Pyrophorics shall not be stored above eye level.

Many pyrophorics are not stable in long-term storage at room temperature and vendors often recommend cooler storage, for example, Sigma recommends 2-8°C for *n*-butyllithium. Manufacturers’ recommendations for storage conditions (e.g. temperature) should always be consulted and followed.

To slow the spread of fire, it is **highly recommended[[4]](#footnote-4)** pyrophoric materials be stored in unbreakable non-combustible secondary containment, i.e. steel cans.[[5]](#footnote-5) If the pyrophoric is in an easily breakable vessel, it is recommended to pack the space between the vessel and the can with vermiculite to provide padding, or at least to have a layer of vermiculite under the inner vessel. Vermiculite has been shown to reduce the intensity of a pyrophoric liquid fire if the vermiculite layer is thick enough to completely contain and cover the liquid in the event of breakage. It is recommended for secondary containment to have a tight-fitting metal lid.

Labelling Secondary containment shall be clearly labelled with the hazards, and if a lid is present, the exterior should also be labelled with the contents. Suitable wording for hazard labelling incudes “air reactive” and/or “pyrophoric”, and if applicable “water reactive” as well.

All primary containers containing pyrophorics should be labeled with the date received and the date opened. For further information, please refer to the [CHP](http://tiny.cc/chem-hygiene-plan) (Section 5) for detailed requirements for hazardous materials labeling.

[Add details of any lab specific labeling requirements, if necessary.]

Personal Protective Equipment Appropriate PPE shall be worn for all work with hazardous materials, in accordance with the USC [Minimum Standard](https://tiny.cc/usc-ppe-standard), [CHP](http://tiny.cc/chem-hygiene-plan), [fact sheets](https://tiny.cc/usc-ehs-fact-sheets), and any Department- or School-specific requirements.

Nomex lab coats shall be worn when working with pyrophorics as they provide the highest level of fire protection. Eye protection shall be worn when working with pyrophoric materials.

Goggles are the appropriate eye protection when liquid pyrophorics are used, or when solid pyrophorics are used in the vicinity of other splash hazards. Wearing a face shield over goggles is recommended for operations of particularly high hazard/risk.

Due to the inherent fire hazard associated with pyrophoric materials, EH&S strongly recommends using high-temperature gloves whenever possible. High-temperature gloves are not chemical resistant, so when they are used, chemical-resistant gloves should be worn over the high-temperature ones.

When working with pyrophorics, it is recommended that personal apparel should be made from natural fibers (e.g., cotton, linen, wool) as opposed to synthetic materials (e.g., polyester, nylon). Common synthetic fibers melt and stick to the skin when exposed to fire, which may exacerbate injury; they also burn energetically.

Leggings and other similarly thin leg coverings provide minimal protection from heat and burns; therefore, it is recommended more protective leg coverings (e.g. cotton trousers) be worn when working with pyrophorics.

Note that for reasons of safety and regulatory compliance, respirator usage is NOT permitted outside of the [USC Respiratory Protection Program](https://tiny.cc/usc-ehs-RPP-fs). Please refer to the [CHP](http://tiny.cc/chem-hygiene-plan) (Section 8) and [EH&S Fact Sheets](https://tiny.cc/usc-ehs-fact-sheets) for additional information about PPE requirements.

[Add details of any lab- or procedure-specific PPE rules/requirements.]

PPE: Gloves In the event of a laboratory incident involving pyrophorics, the most probable location of burn injuries is the hands, and to a lesser extent the forearms. Gloves composed of aramid fibers (Nomex®, Kevlar®, Technora®), thick leather (e.g. welding gauntlets), carbonized fiber (e.g. CarbonX®), or glass fiber all provide some level of fire protection to the hands, and long gloves also protect the forearms. Glass fiber and thick leather gloves have disadvantages making them unsuitable for most lab usage. Furthermore, many high-temperature gloves are too thick to provide adequate dexterity, which increases the risk of accident. However, there are CarbonX® and aramid gloves available which are thin enough to be practical to wear under chemical resistant gloves without excessively impairing dexterity, but which may nonetheless reduce the risk of serious burn injury.

Wearing flame resistant under-gloves is highly recommended for all pyrophoric work except where reduced dexterity makes work impossible or results in increased overall risk.

CarbonX® knitted gloves designed for use as a glove liner are available. Long gloves are preferred to give additional forearm protection over and above that provided by the Nomex lab coat, e.g. [CarbonX® CX10020 Carbon Fiber Knit FR Glove and Sleeve, available here](https://www.magidglove.com/carbonxr-cx10020-carbon-fiber-knit-fr-glove-and-sleeve-cx-100-20).

Thin Nomex® flight/aviator/aviation gloves are widely available (e.g. military surplus stores, Ebay®, aviation stores) and have been used as a glove liner for pyrophoric usage, for example, see [these gloves](https://www.mypilotstore.com/MyPilotStore/sep/8049), or [these gloves](https://marvgolden.com/nomex-flight-gloves-green/).

Do not directly expose high-temperature gloves to chemicals as they are porous, not chemical resistant, and cannot be decontaminated.

Clean-up: General All work areas and equipment is to be cleaned and decontaminated after use. Syringes and other items containing residual pyrophoric materials shall not be left unattended until in a safe condition.

Potentially contaminated PPE shall be removed before entering clean areas. Hands shall be washed before entering clean areas and after completion of work.

[If specific decontamination/cleaning procedures are required please enter details here.]

Clean-up: Alkali metals When alkali metals in oil are cut up on a cutting board, small specks of metal tend to be formed. If the area is subsequently cleaned with paper towels and they are thrown in the trash, there may be spontaneous ignition after a delay. (This is not a hypothetical risk — it has occurred at USC and required LAFD response to extinguish the resulting fire.)

To safely clean-up after cutting alkali metals, first pick up any visible pieces with tweezers and add to the reaction vessel, return to storage, or quench (see below), as appropriate. Potentially contaminated tweezers and cutting blades should be quenched using isopropanol (see below), or if only tiny specks or no visible specks of alkali metals are present, they may be dropped into water. The work area and cutting board should be thoroughly wiped down with dry paper towels, which should immediately be thrown into a bucket of water. (If necessary, use long tongs or a metal pole to completely submerge the towels.) A final thorough wipe-down with paper towels saturated with soapy water completes the cleaning. All the towels should be collected in the water bucket and retained there for at least 24 hours before disposal.

Note: A “classic’ incident is to throw alkali-metal-contaminated paper towels into a sink to quench, only to have the sink erupt in flames because a previous user left ethanol or acetone washings in the sink. (Again, this is not a hypothetical situation.) Always ensure the absence of any flammable solvents or flammable vapors before conducing quenching operations.

When using alkali metals in a glove box, clean-up inside the box using dry tissues. A smear of silicone grease on a tissue can be used to help adhere specks of metal. Have a bucket of water handy and drop the paper into the bucket (using long tongs) immediately upon opening the airlock. If any sizable lumps of alkali metal are present, remove them from the glove box in a sealed container and quench using isopropanol (see below).

Quenching of alkali metals Large quantities of unused alkali metal should be disposed by Hazmat. Small quantities (e.g. up to 1 cu. cm total) can be quenched in the lab by the use of a safe technique.

Quenching should be conducted in a fume hood away from flammable materials. A typical safe technique is to place the alkali metal in a flask or beaker containing about 2-3 cm depth of toluene or xylenes. Cautiously add isopropanol with slow stirring until a steady stream of hydrogen bubbles emanates from the metal. (There may be a delay between adding the first few drops of isopropanol and the evolution of hydrogen, so be patient.) Stirring does not have to continue after the isopropanol is added. Loosely cover the beaker with a watch glass or petri dish to minimize evaporation and leave until all metal has disappeared and no bubbles are visible. (This may take hours — ensure appropriate signage if the reaction is left unattended.) Add a larger volume of isopropanol, ethanol, or methanol (e.g. 1-2 cm depth) with stirring, cover loosely, leave for an hour. At the end of this time, water should be cautiously added with stirring (about 0.5 cm depth is enough), and if there is no sign of reaction or appreciable heat evolution, the solution should be safe to dispose in a non-halogenated organic waste bottle.

If quenching more than few cubic millimeters, use an adequate volume of solvent, keep an eye on the reaction, and replenish with solvent if evaporation occurs.

[Add lab-specific quenching instructions here.]

Clean-up: Liquid pyrophorics To clean syringes and cannulae used with liquid pyrophorics, it is recommended the initial two rinses be done with a non-reactive solvent, which will remove the bulk of the pyrophoric in a diluted form, without potentially producing solid reaction products which might cause blockage, and without producing heat. Petroleum ether, hexanes, cyclohexane, heptane, or toluene are generally suitable for organolithiums whereas tetrahydrofuran (THF) is a good solvent for Grignard reagents. The rinse liquid should be quenched with isopropanol then water (or other quenching agent(s) appropriate for the chemistry of the pyrophoric) before disposal. If the volume of the rinse liquid is sufficient to suitably dilute the pyrophoric, there should be minimal risk of ignition before or during quenching.

After the initial solvent washes, isopropanol (or other quenching agent(s) appropriate for the chemistry of the pyrophoric) should be used to wash the interior of the syringe or cannula to quench pyrophoric traces without risk of blockage or violent reaction.

[Add lab-specific quenching instructions here.]

Quenching of other pyrophorics Other pyrophoric materials (metal hydrides, phosphines, boranes, silanes, etc) should be quenched safely using a procedure taken from the literature or developed in-house by a suitably experienced lab member.

[Specific quenching techniques should be entered here, or referenced here and attached as an appendix.]

Specific dangers to avoid Alkyllithiums are not entirely stable in storage and slowly decompose, typically at a rate of a few hundredths to a few tenths of a percent per month. The decomposition produces an alkene plus lithium hydride in the form of a suspension of extremely small particles. The lithium hydride powder, if sufficient in quantity, can increase the pyrophoricity. Furthermore, while not in itself a safety problem, the decomposition can affect the stoichiometry of reactions, so alkyllithium solutions should be titrated to determine an accurate concentration if this is important.

Many pyrophorics pose potent reactive hazards. For example, alkali metals may ignite or explode on contact with halogenated solvents. Lithium aluminum hydride and sodium hydride may produce violent reaction or thermal runaway with numerous solvents and reactants. Please refer to [Bretherick's Handbook of Reactive Chemical Hazards](https://www.sciencedirect.com/book/9780123725639/brethericks-handbook-of-reactive-chemical-hazards) for details.

Lithium slowly reacts with nitrogen at room temperature, producing a nitride layer which can reduce the reactivity of the metal and interfere with experiments (see [here](https://www.sciencedirect.com/science/article/pii/S0022328X00807123) for an example). When heated, lithium can ignite in nitrogen and burn energetically. For both these reasons, it is recommended to handle lithium metal under argon. (Nitrogen may suffice if the metal is not heated, not in a high-surface-area form such as powder, and if the reduced reactivity is acceptable.)

Molten lithium rapidly attacks glass and causes breakage ([reference](https://www.sciencedirect.com/science/article/pii/S0022328X00807123)). This tends to happen as soon as the lithium “wets” the glass. Therefore, it is highly dangerous to employ glass vessels for any experiment involving molten lithium. Stainless steel vessels are suitable for use with this material.

Potassium is a time-sensitive chemical as it can form an explosive crust in storage. Please refer to the [EH&S website](https://ehs.usc.edu/research/lab/time-sensitive-chemicals/other-time-sensitive-chemicals/) and [CHP](http://tiny.cc/chem-hygiene-plan) for information and details, including specific dating and maximum storage time requirements.

When sodium hydride dispersion in oil is used, the first step is often to wash with a hydrocarbon solvent under nitrogen to remove the oil. If this is done, the washing liquid may ignite when poured into a waste bottle due to residual sodium hydride dust. The washing liquid should be collected under nitrogen and quenched in a safe manner before disposal (e.g. using isopropanol, then once all reaction has ceased a few drops of water should be added).

Storing anhydrous solvents over pyrophoric drying agents is an unsafe practice which caused at least one fire at USC. This practice should be discontinued.

Syringes and pyrophorics Glass syringes with a metal or glass plunger shall not be used with pyrophoric liquids on account of the danger of jamming and because they are not air- or liquid-tight.

(Pyrophoric liquids easily decomposes to metal hydroxides, metal oxides, etc, in the fine gap between the barrel and plunger, irreversibly gluing the syringe together.) Glass syringes with a gas-tight PTFE-tipped plunger may be used, but are not recommended on account of fragility, and because it is too easy to accidentally pull the plunger completely out.

Plastic syringes with a rubber seal are not recommended for pyrophoric applications (or any application with non-aqueous solutions). Typical solvents used with pyrophorics (e.g. hexanes) may cause the syringe to rapidly jam due to both stripping of silicone lubricant and swelling of the rubber.

Syringes constructed entirely from polyethylene or polypropylene (e.g. HSW® Norm-Ject® and Henke-Ject®) are suitable for liquid pyrophorics. For all sizes above 1 mL, Luer-lock needle attachment should be used to prevent accidental needle detachment (e.g. [these syringes](https://www.air-tite-shop.com/p-15-2-part-luer-lock-syringes.aspx)).

Pulling out a syringe plunger too far and spilling the contents is a known serious risk and every effort shall be made to avoid this eventuality. Both the risk (i.e. probability) and hazard (i.e. potential harm done) increases with syringe size; therefore, **syringes of more than 20 mL capacity shall NOT be used with pyrophorics.** It is recommended that any transfer of more than 10 mL be done using a cannula technique employing a measuring cylinder under nitrogen. It is further recommended that syringes are not filled to more than 50% capacity to minimize the risk of accidental plunger detachment.

Due to the spillage risk, it is recommended flame resistant under-gloves be worn when doing any syringe transfer of pyrophoric liquids.

Experimental techniques Appropriate air-sensitive techniques shall be employed when handling pyrophoric materials. Examples of such techniques may be found in the references given at the end of this document. Good technique should be reinforced by effective hands-on training.

When transferring liquids, bottles should be securely clamped to a stand. While bottles may need to be tipped slightly to extract the last few drops, it is hazardous to tip a bottle of pyrophoric liquid to compensate for an excessively short needle. Use a needle or cannula which is long enough to reach the liquid without excessive inclination of the bottle. Under no circumstances shall a bottle of pyrophoric liquid be inclined to the extent that the liquid contacts the septum.

Never attempt to remove pyrophoric liquids from a vessel without first inserting a nitrogen bleed needle.

[Add details of specific experimental techniques or procedures you will be using in the lab under this SOP.]

Waste disposal DO NOT attempt to quench large quantities of pyrophoric materials. If significant quantities of unused pyrophorics need disposal, please place an online Hazmat waste request via EHSA or RSS. If significant numbers of pyrophoric materials need disposal (e.g. as part of an inventory reduction), please contact [hazmat@usc.edu](mailto:hazmat@usc.edu).

Small quantities of pyrophorics (e.g. pyrophoric reaction residues, or residual amounts of pyrophoric liquids in empty reagent bottles) must be quenched according to a recognized safe protocol before disposal in the appropriate waste container (most commonly non-halogenated organic liquid waste).

For more information on waste segregation, labelling, and disposal procedures, please refer to the [hazmat webpages](https://ehs.usc.edu/hazmat/), [fact sheets](https://tiny.cc/usc-ehs-fact-sheets), and [CHP](mailto:CHP). Please email [hazmat@usc.edu](mailto:hazmat@usc.edu) if you have questions that are not answered by EH&S online resources.

[Add details of any lab-specific waste disposal rules.]

Pyrophoric spill response: A pyrophoric liquid spill is “minor” if only a few drops are spilled and fire does not ensue. If a minor spill occurs, wait for the reaction with air to subside. Once no reaction is evident, wipe with a paper towel saturated with soapy water. Keep the wet paper in a beaker of water for observation before disposal as solid chemical waste.

A pyrophoric liquid spill of a few milliliters in an accessible position on a hard surface (e.g. benchtop or floor) is of intermediate hazard. If safe to do so, immediately pour dry sand (or other Class D extinguishant) onto the spill to prevent ignition. If the spill has already ignited, and only if safe to do so, cover with Class D extinguishant or use the appropriate fire extinguisher. (A Class ABC extinguisher is appropriate for many liquid pyrophoric solutions, e.g. butyllithiums, but is unlikely to work for alkylaluminums, which need to be covered in a Class D extinguishant.) Call DPS and request Hazmat assistance. Other than covering with extinguishant, lab personnel should not attempt further spill cleanup themselves.

A pyrophoric liquid spill is “major” if the volume is larger than a few milliliters, or if it is in an inaccessible location (e.g. running under cabinets), or if it is soaking into a porous surface or material. Alert all lab members, evacuate the lab closing the door, and call DPS requesting Hazmat and Fire response. Activate the fire alarm if ignition occurs. During the process of evacuation, dry sand or other Class D extinguishant may be poured over the spill, but only if safe to do so.

Very small solid pyrophoric spills (a few tens of miligrams) may be quenched by application of paper towel saturated with water. (Take care as brief flashes of flame may ensue.) Keep the wet paper towel in a beaker of water for observation before final disposal.

Any larger spill should be covered with dry sand or other Class D extinguishant before calling DPS and requesting Hazmat assistance, and Fire response too if there seems any danger of ignition.

**If pyrophoric material is spilled on an individual, they shall immediately call out for help from nearby lab members and proceed directly to the safety shower. If the individual is on fire, they should immediately drench under the safety shower, even if the pyrophoric is water reactive. If the spill has not yet ignited and is on an easily removable garment (e.g. lab coat), an effort can be made to quickly remove the contaminated garment before ignition occurs, but only if attempting this will not delay getting to the safety shower.**

General spill response Chemical spill clean-up shall not be attempted if lab personnel do not have proper training and experience, necessary spill kit supplies, and appropriate personal protective equipment.

Before starting work, review the [**Spill Response and Clean-Up**](https://ehs.usc.edu/hazmat/spill-cleanup/) web page and Section 10 of the [**CHP**](http://tiny.cc/chem-hygiene-plan). All personnel operating under this SOP shall familiarize themselves with this information and shall re-review these references at least annually.

Please refer to the EH&S [Chemical Spill Kit Guide Sheet](https://tiny.cc/usc-ehs-chmSplkit-gs) for guidance on appropriate spill kit materials.

**Call DPS for all spills, even if they get cleaned up by lab personnel.** DPS will pass information to the EH&S and Hazmat on-call system. If needed, trained staff will be sent to the lab to clean and decontaminate the spill. If lab personnel clean the spill themselves, notification should still be made as lab safety specialists may wish to follow up with a routine safety investigation.

**Spills posing a respiratory hazard SHALL NOT be cleaned by lab personnel. Evacuate the area, restrict access, call DPS.**

Emergency response **Before starting work, review the** [**EH&S emergency notification and incident reporting webpage**](https://tiny.cc/usc-injury), **and the** [**1‑2‑3 poster**](https://tiny.cc/usc-123)**. Ensure that the 1-2-3 poster is posted in the lab.** **All personnel operating under this SOP shall familiarize themselves with these documents and webpage.**

**All personnel operating under this SOP shall have downloaded and read Section 10 of the** [**CHP**](http://tiny.cc/chem-hygiene-plan) (“*Emergency Response / Injury and Illness Reporting*”). This section provides information on chemical exposure response, spill response, and injury reporting.

**The EH&S emergency notification and incident reporting webpage, 1-2-3 poster, and CHP Section 10 are hereby incorporated into this SOP by reference.**

**All personnel operating under this SOP shall have the DPS emergency number programed into their phone** (UPC 213-740-4321; HSC 323-442-1000).

**Phone the DPS emergency line in an emergency!!** DPS have 24 h/day immediate communication access to primary and backup personnel on the EH&S and Hazmat on-call rota. **Do NOT call the EH&S general phone line or individual EH&S personnel in an emergency as timely response is not guaranteed.**

References

1. [*Technical Bulletin AL-134: Handling Air-Sensitive Reagents*](https://www.sigmaaldrich.com/deepweb/assets/sigmaaldrich/marketing/global/documents/685/583/al_techbull_al134.pdf), Sigma-Aldrich (Millipore Sigma). Useful document giving detailed guidance on techniques for transferring air-sensitive liquids using syringes and cannulae. Illustrated with clear diagrams and photographs. Recommended reading for all persons using air-sensitive reagents, or who purchase reagents in bottles fitted with a rubber septum (e.g. Aldrich® Sure/Seal™ bottles).
2. [*DOE Handbook: Primer on Spontaneous Heating and Pyrophoricity*](https://www.standards.doe.gov/standards-documents/1000/1081-BHdbk-2014/@@images/file) (DOEHDBK-1081-2014).
3. [*Handling Pyrophoric Reagents*](http://www.pnl.gov/main/publications/external/technical_reports/PNNL-18668.pdf), DOE (PNNL-18668). An important resource for dealing with some of the practical aspects of safe handling of pyrophorics in a research lab. It should be read by all pyrophorics users.
4. [*On the pyrophoricity, safety, and handling of metalorganic chemicals*](http://www.sciencedirect.com/science/article/pii/S0022024806010189). This reference is concerned with organometallic compounds used in CVD, such as trimethylaluminum. It contains useful experimental results on the resistance of PPE to pyrophoric materials, and on this account should be read by all users of pyrophoric liquids. Additionally, Figures 1-3 in the paper graphically show the effect of pouring a pyrophoric liquid into air, and show the burns which pyrophoric liquids can produce on PPE.
5. [*Methods for the safe storage; handling; and disposal of pyrophoric liquids and solids in the laboratory*](http://www.sciencedirect.com/science/article/pii/S1871553210000289). An important resource for dealing with some of the practical aspects of safe handling of pyrophorics in a research lab. It should be read by all pyrophoric users. (Not available at USC except via interlibrary loan; however, a free word manuscript version is online [here](https://sti.srs.gov/fulltext/SRNS-STI-2010-00057.pdf).)
6. [*Lab safety, PPE, and pyrophoric liquids*](http://www.sciencedirect.com/science/article/pii/S1871553209000838). Short, but informative article.
7. [*Safe handling of organolithium compounds in the laboratory*](https://doi-org.libproxy2.usc.edu/10.1016/S1074-9098(02)00295-2). This reference is not as up-to-date as some of the other resources, but much of the information on hazards, properties, and stability and decomposition of organolithium compounds is useful. Note that the recommendation for safety glasses and for using nitrile gloves is no longer considered sufficient when handling liquid pyrophorics (goggles are required; flame resistant gloves are recommended to be worn under chemical resistant gloves).
8. [*Improved Safety during Transfer of Pyrophoric tert-Butyllithium from Flasks with Protective Seals*](https://pubs.acs.org/doi/10.1021/acs.oprd.8b00151). Double-ended transfer vial technique to reduce risk during transfer of small quantities of maximum-hazard liquid pyrophorics.
9. [Bretherick's Handbook of Reactive Chemical Hazards.](https://www.sciencedirect.com/book/9780123725639/brethericks-handbook-of-reactive-chemical-hazards) The most extensive compilation of chemical incompatibilities and reactive hazards. Recommended to refer to this reference before using highly reactive reagents.
10. Book: *The Manipulation of Air-Sensitive Compounds*, Duward F. Shriver and M. A. Drezdzon, 1986 (2nd edition), Wiley, ISBN: 978-0-471-86773-9. This book is [available from the publisher](https://www.wiley.com/en-us/The+Manipulation+of+Air+Sensitive+Compounds%2C+2nd+Edition-p-9780471867739) at high cost, but is also widely available at reasonable cost from second-hand retailers.

SOP Acknowledgement

The undersigned acknowledge by their signature that they:

1. Have read, understood, have access to, and agree to abide by this SOP, AND;
2. Have read and understood the emergency response resources incorporated into this SOP by reference (“[**1-2-3 poster**](https://tiny.cc/usc-123)”, **[CHP Chapter 10](http://tiny.cc/chem-hygiene-plan)**, and [**EH&S emergency notification and incident reporting webpage**](https://tiny.cc/usc-injury)), AND;
3. Will download, store, read, and thoroughly familiarize themselves with safety data sheets (SDSs) for all the hazardous materials they intend to use within the scope of this SOP.

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| **Name** | **USC ID** | **Email** | **Signature** | **Date** |
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Internal Training Record

If hazards are high or complex, or personnel have limited prior experience or training, then hands-on training should be provided on the contents of this SOP. For convenience, the training may be documented using this form, although PIs are free to keep internal training records in other formats if desired. Training may be conducted by the PI, or the PI may delegate a suitably experienced and knowledgeable lab member (e.g. lab manager or senior postdoc) as the trainer. If delegated, the PI still retains management responsibility for the quality and adequacy of the safety training.

|  |  |  |  |
| --- | --- | --- | --- |
| Trainer name |  | Trainer position |  |
| Trainer USC ID |  | Trainer email |  |
| Trainee #1 name |  | Trainee #1 USC ID |  |
| Trainee #1 email |  | Trainee #1 signature |  |
| Trainee #2 name |  | Trainee #2 USC ID |  |
| Trainee #2 email |  | Trainee #2 signature |  |
| Trainee #3 name |  | Trainee #3 USC ID |  |
| Trainee #3 email |  | Trainee #3 signature |  |
| Trainee #4 name\* |  | Trainee #4 signature |  |
| Trainee #4 email |  | Trainee #4 USC ID |  |
| Date training started |  | Date training completed |  |
| Type of training (delete as appropriate) | **Initial training**  **Refresher training** | Type of training (delete as appropriate) | **Classroom training**  **Hands-on laboratory training** |
| If refresher training, provide date of initial training |  | If refresher training, was the initial training hands-on in the lab? | **YES 🞏 NO 🞏** |
| Signature of trainer confirming the above named trainees have successfully completed safety training on the contents of this SOP (and any additional subjects listed below) | |  | |
| Date of signing by trainer | |  | |
| Additional subjects covered by safety training |  | | |
| \* If there are more than four trainees, please append an additional sign-in sheet. | | | |

1. According to OSHA, a self-heating chemical “*…by reaction with air and without energy supply, is liable to self-heat; this chemical differs from a pyrophoric liquid or solid in that it will ignite only when in large amounts (kilograms) and after long periods of time (hours or days)*.” [↑](#footnote-ref-1)
2. Potassium and NaK alloy invariably ignite rapidly on contact with water. Sodium may ignite if the quantity of metal is large, the quantity of water is relatively small, or heat dissipation is inhibited, e.g. Na in contact with wet paper towel as opposed to a large volume of bulk water. Lithium has a significantly lower tendency to ignite than sodium, but the heat of reaction with water is extremely large and runaway reaction leading to ignition is possible. All alkali metals are dangerously reactive with a wide range of materials, for example violent ignition or explosion is a usual outcome on mixing an alkali metal with chlorinated solvent. Therefore, all alkali metals including lithium shall be considered as having pyrophoric tendencies and handled as such. [↑](#footnote-ref-2)
3. Please email labsafety@usc.edu for information on suitable specialist Class D extinguishants if handling significant quantities of lithium, metallic lanthanides, powdered Ti/Zr/Hf, trialkyl-Al/Ga/In, or other materials which burn with particularly high energy. Specialist Class D extinguishants include powdered graphite or copper for lithium fires. Sodium chloride is a Class D extinguishant with wide applicability, but unlike dry sand, humidity may cause it to cake into lumps. If used as an extinguishant, it should be periodically inspected to ensure it remains free-flowing. [↑](#footnote-ref-3)
4. This recommendation is likely to be upgraded to a requirement in coming years; therefore, labs with crowded pyrophorics storage locations (especially refrigerators) should plan ahead for the increased storage volume requirements which may result from moving all the pyrophorics into steel secondary containers. If large quantities of pyrophorics are currently present and there is insufficient space to fit steel secondary containers, an inventory reduction should be the first approach considered. [↑](#footnote-ref-4)
5. Chemical suppliers often use steel cans as secondary packaging on their products; these cans may be conveniently repurposed as secondary containment for pyrophorics. Alternatively, steel cans (with the advantage of reusable lids) are easily found from a variety of sources, for example, Lowes has [1 quart and 1 gallon metal paint buckets with lids](https://www.lowes.com/pl/Paint-bucket--Buckets-Buckets-bucket-accessories-Paint-supplies-Paint/4294625955?refinement=4294689458,4294832948). [↑](#footnote-ref-5)