Chemical Risk Management Protocol

Safe Methods of Use (SMOU)

Pyrophoric Chemicals

Document Owner: Associate Director, Health, Safety and Wellbeing
Content Manager: Manager, Hazard and Containment
Version: 1.0
Issue Date: May 2024

Table of Contents

1 Purpose

This Safe Method of Use (SMOU) applies to principal investigators (PIs), laboratory managers, designated laboratory persons (DLPs), and all staff and students who direct or participate in the use of pyrophoric chemicals at the University of Auckland.

2 Disclaimer

Safety Data Sheet (SDS) Databases should be consulted for specific information about the compound you will be using. Gold FFX SDS Database is available on the Library database. Instructions on how to source this information can be found on the Health, Safety and Wellbeing Databases website:

https://www.auckland.ac.nz/en/health-safety-wellbeing/health-safety-topics/laboratory-safety/chemical-safety/databases.html

Please read this SMOU in conjunction with the Chemical Risk Management Guidelines.

Note: 'Shall' denotes a mandatory requirement and 'should' denotes a recommendation.

3 Training and Competency

University personnel shall not use pyrophoric reagents until they have:

1. Read and fully understood these safe operating procedures
2. Had hands-on documented training and supervision in pyrophoric material use
3. Performed a risk assessment. Specific hazards may demand further safety measures.

New users of pyrophoric reagents shall work under the close supervision of an experienced user until the Responsible Principal Investigator is satisfied, they can work with these compounds in an unsupervised manner.

A risk assessment shall be undertaken prior to purchase or use of pyrophoric materials.

4 Classification and Description

Pyrophoric chemicals usually fall under UN Class 4.2, as shown in the table below.

UN Class	HSNO Class	Corresponding GHS 7 Class
4.2 Substances liable to spontaneous combustion	4.2A	pyrophoric liquids Category 1, or pyrophoric solids Category 1
	4.2B/C	self-heating substances and mixtures Category 2/3

A variety of solids are pyrophoric (spontaneously ignite in air) including but not limited to:

- Finely divided metals (bismuth, calcium, hafnium, iron, magnesium, titanium, uranium, zirconium)
- Alkali metals (lithium, sodium, potassium, especially sodium potassium alloy – NaK, and even more dangerous are cesium and rubidium)
- Low valent metal halides (titanium dichloride)
- Metal hydrides (potassium hydride, sodium hydride, lithium aluminium hydride - LAH, uranium trihydride)
- Non-metal hydrides (arsine, boranes, germane, phosphine, silane) (Most of these are actually gases.)
- Alkylated derivatives of metal and non-metal hydrides (diethyl aluminium hydride, diisobutylaluminum hydride (DIBAL), Red-Al, dichloro(methyl)silane) (Usually in liquid form or in solution.)
- Alkylated metals (butyl lithium, triethylboron, trimethylaluminum, diethylzinc) (Usually in liquid form or in solution.)
- Alkylated metal alkoxides or halides (dimethylaluminium chloride, diethylethoxyaluminium)
- Metal carbonyls (dicobalt octacarbonyl, nickel carbonyl)
- Used hydrogenation catalysts, e.g. Raney Ni, are especially hazardous due to adsorbed hydrogen
- Copper fuel cell catalysts, e.g. Cu/ZnO/Al2O3, Methanetellurol (CH3TeH)
- Finely divided Iron sulfides (FeS, FeS2, Fe3S4), Potassium sulfide (K2S), Aluminium phosphide (AlP)

5 Hazards

In general, pyrophoric materials ignite spontaneously when exposed to air.

Pyrophoric materials also tend to be associated with flammable solvents. Other hazards include corrosiveness, water reactivity, peroxide formation, and toxicity.

BEFORE working with pyrophoric reagents, read the relevant Safety Data Sheets (SDS) and understand the hazards. The SDS shall be reviewed before using an unfamiliar chemical and periodically reviewed as a reminder.

6 Safe Use

6.1 PPE

Eye Protection

a) Chemical splash goggles or safety glasses shall be worn whenever handling pyrophoric chemicals.

b) A face shield is required any time there is a risk of explosion, large splash hazard or a highly exothermic reaction. All manipulations of pyrophoric chemicals which pose this risk shall occur in a fume hood with the sash in the lowest feasible position. Blast shields are advised as these provide protection for all laboratory users.

Skin Protection

a) Gloves shall be worn when handling pyrophoric chemicals. Nitrile gloves should be adequate for handling small quantities of most of these, however they are combustible. Suitable chemical-resistant gloves are required for working with large quantities.

b) A flame-resistant lab coat shall be worn.

c) A chemical-resistant apron worn over the lab coat is required for working with large quantities.

6.2 Safety equipment

1. Eye wash

Suitable facilities for quick drenching or flushing of the eyes shall be within 10 seconds travel time for immediate emergency use.

2. Safety Shower

A safety or drench shower **shall** be available within 10 seconds travel time from where pyrophoric chemicals are used.

3. Fume hood

Many pyrophoric chemicals release noxious or flammable gases and should be handled in a laboratory fume hood.

4. Fire Extinguisher

a) A dry powder fire extinguisher **shall** be available within **the immediate area** where pyrophoric chemicals are used.

b) A container of dry sand shall be kept within easy reaching distance when working with a pyrophoric material.

5. Glove (dry) Box

Glove boxes are an excellent device to control pyrophoric chemicals when inert or dry atmospheres are required

Note: When absorbent materials are used to clean up contamination from pyrophoric products within a glove box, ensure any residual pyrophoric chemicals are quenched before removal from the glove box

7 Storage

a) Store pyrophoric chemicals under an inert atmosphere or under kerosene as appropriate.

b) Avoid storage areas with heat/flames, oxidisers, and water sources.

c) Containers carrying pyrophoric materials shall be clearly labelled with the correct chemical name and hazard warning.

8 Quenching of residual pyrophoric materials

Before starting work with pyrophoric materials, ensure you have identified a safe method of quenching the residual materials. Considerations should include:

- Appropriate solvents to dilute with, and correct order of addition
- Cooling methods
- Ensuring adequate supervision, not working alone.

DO NOT attempt to quench large amounts of pyrophoric materials – leave it to professional disposal companies.

9 Disposal of Pyrophoric Solid Reagents as Hazardous Waste

- Pyrophoric chemicals should be disposed of as hazardous waste through the University's hazardous waste contractor.
- Carefully package and clearly label the wastes.
- Specifically tell the chemical waste contractor that the materials are pyrophoric, to ensure they provide staff with correct handling expertise.
- **DO NOT** attempt to quench large amounts of pyrophoric materials – leave it to professional disposal companies.

10 Emergency Procedures

10.1 Large Spills

a) Exercise extreme caution due to potential spontaneous combustion, and ignition of flammable solvents or other materials.

b) If anyone is exposed, or on fire, wash with copious amounts of water, ideally in the lab shower.

c) Call 111 for emergency assistance.

d) Evacuate the spill area.

e) Post someone or mark-off the hazardous area with tape and warning signs to keep other people from entering.

f) Provide emergency personnel with technical advice on the chemicals involved.

10.2 Small Spills

a) Exercise extreme caution due to potential spontaneous combustion or potential ignition of flammable solvents or other materials.

b) If anyone is exposed, or on fire, wash with copious amounts of water, ideally in the lab shower.

c) Call for a co-worker to provide backup.

d) Place a fire extinguisher nearby.

e) Carefully remove nearby flammable materials.

f) Dry sand should be used to completely smother and cover any spill that occurs.

g) **Carefully** quench; seek expert advice.

h) After complete quench, double bag spill residues for hazardous waste collection.

i) Call 111 for emergency assistance if necessary.

11 Protocols for Use of Pyrophoric Chemicals

The following are suggested methods of handling that can be incorporated into a risk assessment which considers in more depth the specific tasks and materials in use.

11.1 Handling Pyrophoric Liquids

1. The fume cupboard working area shall be clear and free of easily flammable materials such as paper towels and solvents in bottles etc.

2. Securely clamp the bottle and place a containment tray beneath the bottle.

3. If using a cold bath, a dry ice/isopropanol mix should generally be used.

4. Insert the nitrogen inlet needle through the septum/sure seal on the top of the bottle, making sure that the needle sits well above the surface of the liquid.

NOTE the nitrogen inlet should be connected to a properly working oil bubbler to ensure the bottle is not pressurised to any extent with nitrogen gas.

5. Draw nitrogen into the luer-locked syringe being used and expel the nitrogen to the atmosphere three times to make sure that there is no oxygen in the syringe.

6. Insert the syringe needle through the septum/sure seal and into the bottle well below the surface of the chemical. Holding the needle and syringe together and being very careful not to twist it so the luer-locked needle comes loose, slowly pull back the plunger, drawing the chemical into the syringe.

7. If excess solution is accidentally drawn into the syringe then BEFORE REMOVING the syringe from the bottle, simply expel the excess solution back into the bottle until the exact amount required is in the syringe. Make sure the needle remains well under the surface of the liquid while you are doing this.

8. The needle is then drawn above the surface of the chemical, still in the bottle under inert atmosphere. The plunger is drawn back again to fill the top of the

syringe with inert gas. This will ensure that when the syringe is drawn out, the chemical will not be accidentally expelled.

9. Taking care that the plunger of the syringe does not move at all, the syringe needle is then removed from the bottle and the liquid in the syringe is immediately dispensed into the reaction flask which is already under an inert atmosphere (nitrogen or argon). To do this the plunger is slowly and steadily depressed until it reaches the bottom of the syringe barrel.

10. There will always be a small amount of liquid left in the syringe luer-lock assembly and needle after the plunger is depressed. Therefore, this needs to be neutralised immediately after the solution has been dispensed. To do this, the syringe needle is immersed in an inert solvent (e.g. dry THF if the pyrophoric material is n-butyl lithium solution) and the syringe is filled with this inert solvent. The syringe needle is then immersed beneath the surface of another solution of the same dry inert solvent which contains a very small amount of a chemical that can neutralise the pyrophoric compound (e.g. THF containing a very small amount of isopropanol for n-butyl lithium neutralisation). The syringe plunger is slowly depressed to expel the solution. This procedure is repeated at least two more times.

11. The nitrogen line can then be removed from the bottle. The sure seal should be resealed with parafilm to cover the puncture sites created by the needles. This will help ensure that the bottle remains under an inert atmosphere.

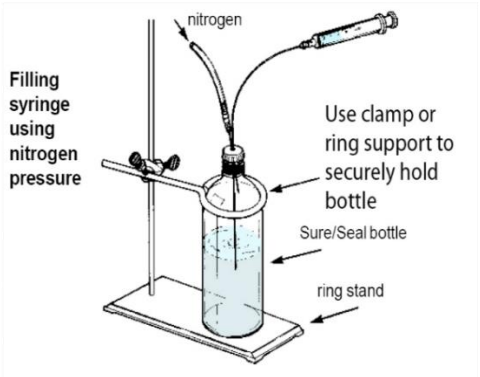

FIGURE 1. SET UP TO FILL SYRINGE WITH A PYROPHORIC REAGENT

11.2 Transferring and Weighing Pyrophoric Solids

a) Set up all necessary experimental equipment first to minimise exposure of pyrophoric solids to air.

b) AVOID rinsing pyrophoric solids with low boiling solvents such as ether or pentane that tend to condense water upon evaporation.

11.2.1 Weighing alkali metals

Before using alkali metals, perform a risk assessment that covers safe methods of cutting and weighing without exposing the metal to the air. While it may be safe to use a knife and tweezers, be aware that incorrect practices particularly for potassium metal may result in explosion.

11.3 Recommendations for Working with Specific Pyrophoric Reagents

a) Lithium Aluminium Hydride (LAH) reacts violently with water, producing hydrogen and large amounts of heat. Therefore, **DO NOT** add anhydrous solvent to LAH. Instead, slowly add LAH to anhydrous solvent in the reaction flask. The initial small amount of LAH will react with any trace amounts of water in the "anhydrous" solvent.

b) Potassium metal is considerably more reactive than lithium or sodium and is potentially very hazardous. Potassium metal can easily be mistaken for sodium metal, so it is essential all labelling is very clear.

c) Potassium metal oxidizes to potassium oxide (K2O), potassium peroxide (K2O2), and potassium superoxide (KO2). The yellow peroxides are shock-sensitive and can explode when handled or cut. Therefore, dispose of potassium metal as hazardous waste if old or if significant amounts of the yellow crust are visible.

d) The mineral oil of potassium hydride or sodium hydride dispersions can be rinsed off using a light hydrocarbon solvent such as heptane. This is easily accomplished in a glove box or can be done in a fume hood **UNDER CAREFULLY CONTROLLED CONDITIONS**. Weigh out the desired amount of the hydride dispersion and place in a flask under a nitrogen atmosphere that is controlled by an oil bubbler. Add dry heptane via syringe, swirl, and let metal hydride settle. Slowly remove the heptane while maintaining the inert atmosphere using a syringe. Then carefully discard the heptane into a separate flask containing isopropanol. Repeat rinse procedure.

e) **AVOID** low boiling rinses such as ether and pentane that tend to condense water upon evaporation.

f) Sodium or potassium amalgam shall not be made without approval from the Hazards and Containment Manager.

g) A sealed glove (dry) box should be used when handling compounds of Trimethyl aluminium.

h) Mildly pyrophoric solids (such as lithium aluminium hydride and sodium hydride) may be handled in the air for brief periods of time, but the containers shall be flushed with inert gas before storage in a desiccator.