UNIVERSITY OF UTAH Department of Chemistry

Safety Manual

Revised: June 2019

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Section 1: Chemical Hygiene Plan

I. Introduction

A. Policy

It is the policy of the University of Utah to provide a safe and healthy workplace in compliance with the Occupational Safety and Health Act (OSHA) and regulations of the Department of Labor including 29 CFR §1910.1450 "Occupational Exposure to Hazardous Chemicals in the Laboratories". This requires, amongst other things, the development of a departmental chemical hygiene plan.

B. <u>Purpose</u>

This document constitutes the Chemical Hygiene Plan (CHP) for the Department of Chemistry at the University of Utah, as required by the aforementioned regulation. Its purpose is to describe proper general practices, procedures, equipment, and facilities to be followed/used by all personnel (employees, PIs, teaching assistants, students, and visitors) working in each laboratory within the department. This is to protect them from potential health hazards while working with chemicals, and to keep the potential for exposure at a minimum. It is the responsibility of the administration, principal investigator, faculty, and research personnel to know and follow the plan.

This document is not intended to cover all hazards found in the department, but instead is intended as an introduction to the most common hazards that a person might encounter. It is important that each group (research group, laboratory class, etc) develop and maintain a chemical hygiene plan that covers the specific hazards present in that group or class. Each group is also required to develop Standard Operating Procedures and document all lab specific trainings.

C. Personnel Covered by this Plan

This Chemical Hygiene Plan applies to all work involving hazardous substances that is conducted within the space assigned to the Department of Chemistry. All researchers and visitors who are conducting research within the Department of Chemistry laboratories must undergo Chemical Hygiene Training as outlined in Part III and submit proof of completion to prior to commencing work.

D. Instructions for the Use of the Safety Manual

The Chemical Hygiene Plan (Section 1) is required reading for all individuals dealing with hazardous chemicals including all laboratory teaching assistants in Department of Chemistry. Section 2: Working with pyrophorics and lasers is provided as a resource available as optional additional lab specific training. Supervisors may assign those portions that are relevant to their specific lab and document that the reading is complete. Alternatively, portions of this section may also be used in the creation of lab specific hygiene plans.

E. <u>Acknowledgement</u>

Portions of the Chemical Hygiene Plan were drawn from "Prudent Practices in the Laboratory: Handling and Management of Chemical Hazards," (National Academy Press, Washington, D.C., 2011). Chemical Hygiene Plans from chemistry departments at MIT, Caltech, UCLA, and the University of Minnesota were also consulted.

II. Responsibility, Authority, and Resources

A. Safety Committee

The safety committee assists the Department Chair with the development and implementation of the Departmental Chemical Hygiene Plan. The committee is also responsible working with OEHS, providing advice and assistance to personnel on various OEHS matters. These include: regular meetings with safety officers from every group, investigating accidents and near misses, administrating a lab inspection program, and recordkeeping of inspection, training, and reports for the department.

> Members of the Chemistry Department Safety Committee (2017) Holly L. Sebahar, chair (<u>holly.sebahar@utah.edu</u>) Richard Ernst (<u>ernst@chem.utah.edu</u>) Jim Muller (<u>jmuller@chem.utah.edu</u>) Agnes Szarzec Larsen (a.szarzec.larsen@utah.edu) Sushma Saraf (<u>s.saraf@utah.edu</u>) Ryan Deluca (<u>r.deluca@utah.edu</u>) Ryan Looper (r.looper@utah.edu) Safety Committee Email address: chemsafetycommittee@lists.utah.edu

B. Supervisors

Supervisory responsibility falls on the principal investigators (PIs), as well as the following departmental personnel:

Undergraduate Laboratory Classes	Course Instructor	
Outreach	Tom Richmond (richmond@chem.utah.edu)	
	Holly Sebahar (holly.sebahar@utah.edu)	
High School Program	Jeff Statler (statler@chem.utah.edu)	
Instrumentation Facilities	Jim Muller (jmuller@chem.utah.edu)	
NMR facilities, including Gauss House	Peter F. Flynn (<u>peter.flynn@utah.edu</u>) -6-	

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Machine Shop	Dennis Romney (romney@chem.utah.edu)
Glass Shop	Kevin Teaford (<u>kteaford@chem.utah.edu</u>)
Electronic Shop	Michael Scott (mike.scott@utah.edu)
X-Ray Laboratory	Ryan Vanderlinden (ryan.vanderlinden@gmail.com)

The primary responsibility of the supervisor is to ensure that the Chemical Hygiene Plan is implemented and to ensure compliance with the OSHA Laboratory Standard. This includes (but is not limited to):

- 1) Ensure that all personnel comply with the departmental CHP and do not operate equipment or handle hazardous chemicals without proper training and authorization.
- 2) Develop a lab specific chemical hygiene plan. Maintain documentation that states that all personnel have read and will comply with the lab specific CHP. Ensure compliance.
- 3) Review and approve standard operating procedures (SOPs) for work with hazardous chemicals or dangerous procedures.
- 4) Maintain documentation on all safety trainings.
- 5) Ensure that proper PPE is available and properly used by all personnel and visitors.
- 6) Define the location of designated areas for work with particularly hazardous substances (see section III.D) and ensure the proper inventory of these chemicals.
- 7) Ensure that authorized visitors follow the rules and assume responsibility for visitors' actions and safety.
- 8) Assist and cooperate with OEHS when necessary.
- 9) Formulate procedures for dealing with accidents that may result in the unexpected exposure of personnel or the environment to toxic substances.
- 10) Investigate accidents and near misses and report them to the safety committee.
- 11) Report to the safety committee incidents that resulted in large exposure of chemical substances.
- 12) Take action to correct work practices and conditions that may result in the release of toxic chemicals and/or accidents.
- 13) Instruct personnel to properly dispose of unwanted and/or hazardous chemicals.
- 14) Provide annual refresher safety training that is tailored to the group's safety needs, and maintain careful documentation of these trainings.
- 15) Arrange for non-lab personnel to be informed of potential hazards, and instruct them on how to minimize risks.
- 16) Be a safety role model to personnel.
- 17) In an evacuation to work with the safety officers to: i) account for all personnel; ii) to check assigned building areas are evacuated; iii) to ensure that all equipment, reactions, etc. are shut off or in a stable state upon evacuation of the labs; iv) to check in with the area leader.

C. Groups Safety Officers

Each research group within the department of chemistry must have one assigned safety officer (graduate student or post doc), as well as a vice safety officer. These are assigned annually. The responsibilities of the primary and vice safety officers are as follows:

- 1) To advise and assist lab supervisors in training of new personnel.
- 2) To attend regular meetings with other group safety officers and the safety committee, and to disseminate safety knowledge.
- 3) To evaluate and make safety recommendations to the safety committee.
- 4) To inspect and ensure proper function of group safety equipment, such as spill kits, fire *extinguishers*, eyewash stations, and safety showers.
- 5) To inspect/test peroxide forming chemicals and other potentially dangerous chemicals and to dispose of them accordingly.
- 6) To be in charge of chemical waste and pick-up.
- 7) To enforce the CHP, and report unsafe practices to the lab supervisor (PI).
- 8) In an evacuation, to aid the supervisor in: i) accounting for all personnel during an evacuation; ii) to check assigned building areas are evacuated; iii) to ensure that all equipment, reactions, etc. are shut off or in a stable state upon evacuation of the labs; iv) to check in with the area leader.

D. <u>Research Personnel</u>

Research personnel must follow the CHP along with any additional regulations set by the supervisors (i.e., group safety manuals). Research personnel, as defined by the CHP, are those working under the direction of the supervisor. Visitors (including employees, staff, and students from other research groups) must also follow the CHP and additional regulations set for the space. It is the responsibility of all research personnel to:

- 1) Read, understand, and follow all safety rules and regulations of the CHP and additional, lab-based regulations.
- 2) Plan and conduct all experiments in accordance with the CHP.
- 3) Promote good housekeeping practices in the lab.
- 4) Communicate pertinent portions of the CHP to others in the work area (particularly new researchers or undergraduates).
- 5) Notify the group safety officer and/or supervisor of any hazardous conditions or unsafe work practices.
- 6) Use appropriate PPE at all times.
- 7) Immediately report any job-related illness or injury to the supervisor.
- 8) Immediately report any accidents, incidents, and near misses to the supervisor.

E. Occupational and Environmental Health and Safety Office (OEHS)

The Occupational and Environmental Health and Safety Office (<u>oehs.utah.edu</u>) is responsible for control, review, disposal, monitoring, and advice with respect to work with chemicals and biological agents used in research and teaching. They are responsible for fire extinguisher training, aid the department in chemical hygiene training, and also offer more advanced safety training as needed. They can be reached for advice or assistance, particularly as it involves exposure to chemicals, fire, or other accidents.

Key OEHS Personnel (2016)

OEHS Office	801.581.6590	8am-5 pm Monday-Friday
	801-585-2677	Non-emergencies after hours
		questions@OEHS.utah.edu
James Stubbs, Associate Director	801-585-5788	james.stubbs@ehs.utah.edu
Brandon Newell, Dept. of Chem Contac	t 801-581-8024	brandon.newell@oehs.utah.e
Clint Haymond, Fire Marshall	801-585-9122	Clint.Haymond@ehs.utah.edu
Greg Walters, Hazardous Materials	801-581-5450	gregory.walters@oehs.utah.edu

III. Information and Training

A. Initial Training

Prior to commencing work in any lab, all personnel must complete the following safety training:

1. Graduate students, Postdocs, and long-term (6+ month) visitors:

a) Attendance and participation in the Chemistry Department Safety Course (includes fire extinguisher training and OEHS Chemical Hygiene Training). This training is held annually in August. If attendance is not possible, one must view the online safety videos available on Canvas.

b) Reading the entire Department of Chemistry Chemical Hygiene Plan.

c) Lab-specific training indicated by the supervisor including review of the lab specific chemical hygiene plan and relevant standard operating procedures (SOPs).

2. Undergraduate Researchers and Short-term visitors (< 6 months):

a) Reading portions of the departmental chemical hygiene plan indicated by the Supervisor.

b) Lab-specific training as outlined by the Supervisor.

c) Summer REU students must also attend the safety training, and watch a DOW video.

B. <u>Refresher Training</u>

At least once a year each research group should have a safety refresher meeting that covers topics pertinent to the lab. This can take the form of a game, discussion on near misses or "what if" scenarios, etc. It is recommended that research groups additionally discuss safety at their group meetings.

C. Documentation of Training

<u>All training must be documented</u>. Documentation should include a description (date, title, who gave the training, date, and printed names of those who attended. *A signature* of each attendee is also required to certify training was completed. A training log template is available on the Canvas Safety Site in the Forms folder.

Personnel are required to complete the "Departmental Chemical Hygiene Plan Completion Form" found in Appendix A and in the Canvas Safety Site forms folder once they have read the Departmental Chemical Hygiene plan and prior to working in the lab. Note that you must sign the form, scan it (you may choose to use a free app such as Tiny Scanner or Genius Scan if you do not have access to a scanner) then upload into the Departmental Chemical Hygiene Plan Completion Form Assignment on the Canvas Safety Site.

Lab specific training, including refresher trainings, must be documented and maintained by Supervisors and Safety Officers.

D. Information on Hazardous Substances

It is the responsibility of all researchers to be aware of the health and safety hazards associated with all chemicals involved in their work. Several resources are available to you:

- 1. Safety Data Sheets (SDS), formerly Material Safety Data Sheets (MSDS), that ship with the chemical, and can also be found online at the vendor's website. The more familiar you are with the language of these datasheets, the more useful they will be to you, so it is good practice to look up these sheets for all chemicals in a reaction.
- 2. UCLA has compiled a large database on **standard operating procedures**, or SOPs, for working with chemicals. This can be accessed here: http://www.sop.ehs.ucla.edu/

- 3. Departmental hazardous chemical or procedure **Standard Operating Procedure (SOP) database** stored on the Canvas Safety Site. Here you will find SOPs written by your peers and approved by faculty for use of particular chemicals or processes. If one has not yet been prepared for a chemical (or reaction) that warrants concern, you should prepare one. Blank SOP forms are located in Appendix B and on the Canvas site in the SOP Database folder
- 4. The Department of Chemistry Safety Canvas Site. In this site you will find an Electronic Safety Library Folder containing the titles below as well as other safety related resources and information. Gain access to this site by providing Ms. Lisa Parberry (l.parberry@utah.edu) with your University ID number.
 - *Prudent Practices in the Laboratory:* Handling and Management of Chemical Hazards. Great reference for working with chemicals, quenching reactive species, how to cleanup spills, understanding the various hazards found in the lab, and for Laboratory Chemical Safety Summaries (LCSSs).
 - *Wiley Guide to Chemical Incompatibilities.* Great resource for checking the compatibility of chemicals and waste.
 - *Destruction of Hazardous Chemicals in the Laboratory.* Reference for how to quench reactive chemicals as part of a reaction sequence so that they can safely be disposed of with the bulk chemical waste of the research group.

IV. Protective Equipment

A. Eve Protection

To minimize the risk of eye injury, all personnel and visitors MUST wear eye protection while in a departmental lab.

Eye protection is required by law (Code of Federal Regulations, Title 29, Section 1910.133) for all personnel working in labs that work with chemicals. This protection is required whether or not one is performing an experiment. Groups that work with chemicals must maintain a supply of safety glasses for visitors near lab entrances, and group members are responsible for enforcing the policy of wearing eye protection whilst in the lab.

Safety glasses can be purchased in the stockroom or from VWR or Fischer Scientific. Groups that work with lasers or other light sources should also have a supply of glasses with the appropriate filters.

Ordinary prescription glasses do not provide adequate protection against injury, as they lack side shields and may break upon impact. If one wears prescription glasses, one can either wear safety goggles on top of the glasses or obtain a pair of prescription safety glasses.

Contact lenses provide no protection against eye injury and are no substitute for safety glasses. Further, if chemicals get in the eye, the lens can trap the chemical and interfere with first aid and eye-flushing procedures (note, the lens may not come out with eye flushing). It is imperative that each lab have an up-to-date list of members who wear contact lenses so that appropriate measures can be taken in an emergency (ie, removal of the lenses).

Goggles offer more protection than safety glasses, and should be worn when carrying out operations that have a high risk of splashing chemicals, flying particles, etc.

Face shields must be worn when there is a risk of explosion. This is also encouraged when working with particularly hazardous chemicals that will cause severe burns upon exposure to skin.

B. Lab coats

All personnel working in the lab must have at least one lab coat that is appropriate for their needs. Lab coats must be worn in the lab at all times.

In most instances, a standard 100% cotton lab coat will be sufficient. These are available for purchase in the chemistry stockroom. Those working with pyrophoric chemicals should also have access to a Nomex flame-retardant lab coat to minimize the risk of catching on fire. These can be purchased from VWR and Fischer.

Lab coats should remain in the lab, and under no circumstances should be worn in the bathrooms.

Lab coats can be laundered on campus (2-day turnaround). Bring a completed campus order form to the basement of the University Hospital, room AA120 between 7AM-3PM (M-F). Lab coats must have pockets emptied and be labeled with the group name. You are responsible for dropping off/picking up laundered coats.

C. Gloves

All personnel working with chemicals must wear gloves to protect themselves from hazards associated with chemicals.

Gloves are to remain in the lab, and under no circumstances should they be worn in the office, hallways, or bathrooms. If one is carrying chemicals from one room to another, then one hand may remain gloved whilst the other is glove-free to open doors. Doorknobs and phones should never be handled with gloves. Other areas, such as computer keyboards, may be deemed "gloved;" this lies at the discretion of each research group and appropriate signage must be provided to ensure compliance by group members and visitors.

In most instances, nitrile gloves will be appropriate, but certain chemicals/reactions may require the use of leather (flame retardant), butyl, silvershield (chemical resistance), or another type of glove. Note, most solvents will eventually permeate and destroy nitrile (and latex) gloves. When working with pyrophorics or other highly flammable materials, leather gloves (worn above (clean) nitrile gloves) should be used. This is because leather is flame retardant. Leather pilot gloves offer great dexterity and come in a variety of sizes, available from amazon.com.

Kevlar or cut-resistant gloves should be worn (above clean nitrile gloves) when handling potentially explosive chemicals/reactions, or when handling broken glass. These can be purchased from VWR, Fischer, or uline.

A Chemical Resistance Guide for gloves by NORTH is provided in Appendix D and as a pdf on Canvas in the Electronic Safety Library.

D. <u>Additional PPE</u>

In certain instances, you may need to use additional or more specialized PPE. This includes the use of blast shields and Kevlar sleeves when working with potentially explosive systems.

E. <u>PPE for your cell phone</u>

If you take your cell phone into the lab, it must be in a Ziploc (or other) disposable plastic bag. This is so that you do not accidentally contaminate it with chemicals from your hands. You can still use the touchscreen and other functions through the bag. When leaving the lab or putting your phone up to your ear, take the phone out of the plastic bag. Treat the bags as you do disposable gloves.

F. Laboratory Hoods

Fume hoods are used as a local exhaust method to control inhalation hazards and also to contain chemicals. *It is strongly encouraged for all personnel to use a lab hood when working with all hazardous substances.*

1. **Operating Instructions**

- Do not use hood for perchloric acid procedures.
- Verify that the fume hood exhaust system and controls are working properly and providing necessary airflow before working in the hood.
 - If in doubt, call OEHS and/or test it using the method described in Prudent Practices in the Laboratory, reproduced in Appendix D.
- When using the hood, the sash glass opening should be kept at a minimum and the hood should not be operated with the sash in the full open position. The glass should be no higher than 18".
- Place chemicals and other materials at least 6" inside the sash.

- Do not restrict air flow inside the hood. Do not put large items in front of the baffles and remove all materials that are not needed for the immediate work. Large apparatus should be elevated on blocks.
- Never place your head inside the hood.
- External air movement can affect the performance of the hood so do not operate near open doors, open windows, or fans. Try to avoid rapid body movements and opening the sash rapidly.
- When working with highly toxic/smelly chemicals, or any other situation when an increased air flow is desirable, hit the "emergency" key on the controller (see below) to increase the flow. When done, hit the "emergency" key again to exit the increased flow situation.
- If the alarm goes off, raise/lower the sash and/or declutter the hood until flow levels return to normal. If this fails, silence the alarm (see below) and notify Facility Operations at 801-581-7221 immediately. *Do NOT work in the hood until flow has returned to normal.*
- For more information on the hoods used in the chemistry department, go to:

http://www.mhzelectronics.com/ebay/manuals/thermo_hamilton_safeaire_fume_hood_man ual.pdf.



2. Monitor/Alarm System



All fume hoods in the chemistry department are equipped with a controller/monitor. Below is a description of the various components, and what to do if an alarm goes off.

• <u>LED Lights (top)</u>

• Green light (Normal) is on when the exhaust flow and face velocity are adequate and the fume hood

is operating safely.

- Yellow light is on when the controller is muted or in setback mode. The display will actually read "mute" or "setback" to indicate the meaning of the yellow light.
- Red light will flash if the controller is in emergency mode and will be continually light when an alarm has gone off. The display screen will indicate this with a message as well.
- <u>Soft Keys</u> (directly below display screen)
 - o Menu (always displayed)
 - Provides access to menus
 - Password protected
 - o Setback (always displayed)
 - Activates the setback or second control set point
 - o Reset
 - Resets alarm light, alarm contacts, and audible alarm when in a latched or non-automatic reset mode. If an alarm is reset before the alarm conditions are exited, the controller will reset the alarm but the alarm mode will be re-entered after the alarm delay (time that flow must be above/below the high/low alarm set point before sounding alarm).
 - Resets emergency function after emergency key has been pressed.
 - Clears displayed error messages.

- o Normal
 - Appears if unit has been placed into setback mode.
 - Returns controller to normal set point.
- <u>Quick Keys</u> (directly below soft keys)
 - o Serve as right and left arrows or to increase/decrease volumes.
- <u>Operator Keys</u> (two keys with pictures)
 - o Mute Key
 - Silences an audible alarm.
 - The alarm will remain silent until the mute timeout value has been reached or until unit returns to normal set point.
 - Pressing this twice will permanently mute the alarm.
 - o Emergency Key
 - Puts the controller into emergency mode. This will maximize the exhaust flow and face velocity by modulating the damper or venture valve to a full open position.
 - "Emergency" will appear on the display, the red alarm light will flash on and off, and the alarm will beep intermittently.
 - To return to normal mode, press the Reset key or the Emergency key again.
- For more information on the controllers, go to:

http://www.tsi.com/uploadedFiles/_Site_Root/Products/Literature/Manuals/FHC50-FHM10-Fume-Hood-Controller-Monitor-6003830-

web(1).pdfhttp://www.tsi.com/uploadedFiles/_Site_Root/Products/Literature/Manuals/FHC 50-FHM10-Fume-Hood-Controller-Monitor-6003830-web(1).pdf

http://www.tsi.com/uploadedFiles/_Site_Root/Products/Literature/Manuals/FHC50-FHM10-Fume-Hood-Controller-Monitor-6003830-web(1).pdf

G. Fire Extinguishers, Fire Blankets, Safety Showers, and Eyewash Facilities

All personnel working with chemicals must know the location of fire extinguishers, safety showers, and eyewash facilities.

V. Classes of Hazardous Substances

Chemicals can be divided into several hazard classes. The hazard class determines how the materials should be stored and handled. All chemical containers, either supplied from a vendor or produced in the lab, must include labels or wording that clearly identifies the hazards associated with that chemical. In addition to the labels, hazard information for the specific chemicals can be found by referencing the Safety Data Sheet (SDS) for that chemical. These are provided by vendors and can also be found online.

All rooms that contain chemicals are marked with yellow Hazard Warning Signs that indicate the types of chemical hazards present, if personal protective equipment is required, if food/drink is allowed, and emergency contact information (Figure 5-1). These signs should be checked annually. To request a new or updated sign fill out the Hazard Warning Signage Questionnaire at http://oehs.utah.edu/resource-center/forms/hazard-warning-signage-questionnaire

There are several classes of hazardous substances. and to streamline classification, the globally harmonized system (GHS) is adapted to classify and label chemicals (available at http://www.unece.org.). The GHS classifies substances by the physical, health, and environmental hazards that they pose, and provides signal words (e.g., Danger), hazard statements (e.g., may cause fire or explosion), and standard pictogram-based labels to indicate the hazards and their severity (Figure 5-2). The pictograms, signal word, and hazard statements are standardized under GHS and should be present on all chemical containers from vendors. The signal words, either "Danger" or "Warning," reflect the severity of hazard posed. Hazard statements are standard phrases that describe the nature of the hazard posed by the material (e.g., heating may cause explosion). These are listed in the SDS of chemicals.







Figure 5-2. GHS pictograms for labeling containers.

A. Flammable, Reactive, and Explosive Chemicals

Flammable Chemicals

Flammable substances are those that readily catch fire and burn in air. They may be solids, liquids, or gases. Common flammable liquids include most lab solvents. An example of a flammable gas is hydrogen. In order for a fire to occur, there must be a fuel, oxygen, and ignition source. The National Fire Protection Association (NFPA) classifies the flammability in five degrees of severity, which is based on the flashpoint. The flashpoint is the minimum temperature at which a liquid has sufficient vapor pressure to form an ignitable mixture in air.

- 0. Will not burn
- 1. Must be preheated for ignition; flashpoint above 93 °C
- 2. Must be moderately heated for ignition; flashpoint above 38 °C
- 3. Ignition may occur under most ambient conditions; flashpoint below 38 °C
- 4. Extremely flammable and will readily disperse through air under standard conditions; flashpoint below 23 °C

See Appendix E for a Table of Fire Hazard Ratings for Common Laboratory Chemicals from Prudent Practices. A more detailed discussion can be found in Prudent Practices section 4.D.1.

Flammables must be stored in flammable cabinets if they container size is greater than 1 gallon (4L), and/or the total volume is more than 10 gallons per room. When working with flammables, a flame-retardant lab coat is recommended. It is advised that all clothing be made of natural fibers (eg, cotton, leather, wool) and synthetic fibers such as nylon and polyester be avoided as they melt and drip onto the skin when they burn.

<u>Reactivity Hazards</u>

Reactive substances are materials that decompose via chemical reaction (with for instance, gases found in air). These materials must be stored in a separate flame-resistant storage cabinet. If refrigeration is required, these chemicals should be stored in lab-grade flame- and explosion-proof fridges/freezers. These substances pose an immediate potential hazard and thus proper storage and training is required for each sub-class (see below).

1) Water Reactives and Pyrophorics

Water reactives are chemicals that react violently with water. Examples include alkali metals (eg, lithium and sodium), some organometallic compounds, and metal hydrides. In some instances, the reaction with water produces hydrogen gas, which ignites or reacts explosively with oxygen from the air.

Pyrophorics are a special class of reactivity hazards. The spontaneously combust upon exposure to air and/or water. Examples include alkyl lithium and Grignard reagents and strong reductants.

2) Incompatible Chemicals

Accidental contact of incompatible chemicals can lead to serious explosions and/or the formation of substances that are highly toxic/flammable. Some chemicals are stabilized, rendering them less

reactive towards other chemicals, and it is up to the researcher to check the label of all chemicals to determine if the chemical is stabilized or not. Accidental contact most often occurs when chemicals are not properly stored and in waste streams.

3) Explosive Hazards

Explosive chemicals are those that decompose under conditions of mechanical shock, elevated temperature, impact, friction, detonation, or other suitable initiation, undergoes rapid chemical change, evolving large volumes of gas. Heat, light, shock, and certain catalysts can all initiate explosive reactions. Certain functional groups are more prone to form explosive compounds, and combining such functional groups in synthesis must be done with caution (Table 5-3). These substances pose an immediate potential hazard and thus proper storage and training is required.

Structural Feature	Compound	Structural Feature	Compound
	Acatalanic companyde		compound
— C≡C−Metal	Metal acetylides	C-N-N-S-N-N-C	Bis-arenediazo sulfides
C_C-X	Haloacetylene derivatives	NN	Trizazenes ($R = H$, CN
	Diazirines	N=N-N=N	High-nitrogen compounds, tetrazoles
CN ₂	Diazo compounds	с_о_о_н	Alkylhydroperoxides
c−n−o	Nitroso compounds	с_со_соон	Peroxyacids
	Nitroalkanes, C-nitro and polynitroaryl compounds		Peroxides (cyclic, diacyl dialkyl)
	Polynitroalkyl compounds	C CO-COOR	Peroxyesters
	And unalled - tota	O O Metal	Metal peroxides, peroxoacid salts
UNU	Acyi or alkyl mtrites	-O-O-Non-metal	Peroxoacids
	Acyl or alkyl nitrates	N—►Cr−O ₂	Aminechromium peroxocomplexes
8		N ₃	Azides (acyl, halogen, nonmetal, organic)
C C 1,2-Epoxides	C-N2+2.	Diazoniumsulfides and derivatives, "xanthates"	
C=N-O-Metal	Metal fulminates or aci- nitro salts	N ⁺ -HZ ⁻	Hydrazinium salts, oxosalts of nitrogenous bases
	Fluorodinitromethyl	-N+-OH Z-	Hydroxylammonium salts
NO ₂	compounds	C-N_2+Z-	Diazonium carboxylates or salts
N-Metal	N-Metal derivatives	(N-Metal)+Z-	Aminemetal oxosalts
		Ar-Metal-X	Halo-arylmetals
N-N-O	N-Nitroso compounds	X—Ar-Metal	· internet in generation
N-NO ₂	N-Nitro compounds	N—X	Halogen azides, N-halogen compounds, N-haloimides
C N=N C	Azo compounds	NF ₂	Difluoroamino compounds
CN=NOC	Arenediazoates	— 0—X	Alkyl perchlorates, chlorite salts, halogen oxides, hypohalites, perchloric acid, perchloryl compounds
C-N=N-S-C	Arenediazo aryl sulfides	SOURCE: Carson and Mumford (2002). F	Reprinted from Hazardous
C-N=N-O-N=N-C	Bis-arenediazo oxides	Chemicals Handbook (Second Edition), Car "Reactive Chemicals", p. 228, Copyright Elsevier.	son, P. and Mumford, C. 2002, with permission fro

4) Azos, Peroxides, and Peroxidizables

Organic azo and peroxides are among the most hazardous substances handled in the lab but are also common reagents. They are generally low-power explosives that are sensitive to sparks, heat, or other accidental ignition. They are far more shock sensitive than TNT.

Many common lab chemicals form peroxides on exposure to oxygen in air. These are classified by how readily they form peroxides (Table 6-2). Compounds that form peroxides on exposure to air include aldehydes, ethers, hydrocarbons with allylic, benzylic, or proargylic hydrogens, conjugated

dienes, enynes, and diynes, and saturated hydrocarbons with exposed tertiary hydrogens 0.....(Table 5-4).

Class A chemicals are those that form peroxides after prolonged storage, especially after exposure to air without concentration. These should be tested for peroxides before using, and discarded 3 months after opening. If possible, they should be stored in an inert environment such as a glovebox or nitrogen-filled dessicator. Note that peroxides will first form near the boundary with air, which often is hidden in the grooves of the cap, and hence could explode upon opening.

Class B chemicals are those that form peroxides that only become hazardous upon concentration by distillation or evaporation. Many of these chemicals can be purchased with inhibitors that react with oxygen and prevent the formation of peroxides. Researchers should check labels to make sure that this indicator is present; the stockroom sells both stabilized and

Class A: Chemicals that form explosive levels of peroxides without concentration Isopropyl ether Sodium amide (sodamide) Butadiene Tetrafluoroethylene Chlorobutadiene (chloroprene) Divinyl acetylene Potassium amide Vinylidene chloride Potassium metal Class B: These chemicals are a peroxide hazard on concentration (distillation/evaporation). A test for peroxide should be performed if concentration is intended or suspected.* (See Chapter 6, section 6.C.3) Acetal Dioxane (p-dioxane) Cumene Ethylene glycol dimethyl Cyclohexene ether (glyme) Cyclooctene Furan Cyclopentene Methyl acetylene Diaacetylene Methyl cyclopentane Dicyclopentadiene Methyl-isobutyl ketone Diethylene glycol dimethyl Tetrahvdrofuran ether (diglyme) Tetrahydronaphthalene Diethyl ether Vinyl ethers Class C: Unsaturated monomers that may autopolymerize as a result of peroxide accumulation if inhibitors have been removed or are depleted^a Acrylic acid Styrene Vinyl acetate Butadiene Chlorotrifluoroethylene Vinyl chloride Ethyl acrylate Vinyl pyridine Methyl methacrylate *These lists are illustrative, not comprehensive. SOURCES: Jackson et al. (1970) and Kelly (1996). Table 5-4: Classes of Chemicals that can form peroxides. From PP page 72.

Ethers containing primary and secondary alkyl groups (never	
 distill an ether before it has been shown to be free of peroxide) Compounds containing benzylic hydrogens Compounds containing allylic hydrogens (C=C—CH) Compounds containing a tertiary C—H group (e.g., decalin and 2,5-dimethylhexane Compounds containing conjugated, polyunsaturated alkenes and alkynes (e.g., 1,3-butadiene, vinyl acetylene) Compounds containing secondary or tertiary C—H groups adjacent to an amide (e.g., 1-methyl-2-pyrrolidinone) 	unstabilized THF and ether. It is recommended that researchers use stabilized reagents when possible, and that if these are not available, that they add a small amount (~ 10-250 ppm) of BHT (dibutylhydroxytoluene) to the bottle.

It is recommended that class B chemicals be tested every 3 months for peroxides.

Class C chemicals are monomers that form peroxides that can initiate explosive polymerization. Inhibited monomers should be tested and discarded after 12 months. Uninhibited monomers should be discarded within 24 hours of opening.

5) Other Oxidizers

Oxidizing agents can react violently when they come into contact with reducing materials and sometimes ordinary combustibles. These oxidizing agents include halogens, oxyhalogens, and organic peroxyhalogens, chromates, and persulfates as well as peroxides. In general, inorganic peroxides are stable, but they may form organic peroxides and hydroperoxides in the presence of organics, react violently with water (alkali metal peroxides), and form superperoxides and oxonides (alkali metal peroxides). Perchloric acid is a powerful oxidizing agent and perchloric salts are explosive. Several baths to clean glassware, including pyranna and aqua regia, are strongly oxidizing.

B. <u>Nanomaterials</u>

The health effects of nanomaterials has not been thoroughly investigates. Thus, the uncertainty surrounding the toxicity of nanomaterials merits a cautious approach when working with them. Nanomaterials are any materials or particles with external dimensions of 1-100 nm. Work with nanomaterials requires additional training.

C. Biohazards

It is the responsibility of independent researchers to know the classifications and appropriate safety procedures when working with biological agents. There are several resources available to help identify whether additional steps and safety practices are required outside of the normal chemical hygiene training received within the Department of Chemistry. General information and details can be found on the OEHS site: http://oehs.utah.edu/topics/biosafety. Additionally, the following joint CDC/NIH publication is the primary resource that details the appropriate practices in Biosafety and (affectionately Microbiological Biomedical Laboratories known and as BMBL): http://www.cdc.gov/biosafety/publications/bmbl5/, available in the electronic library on Canvas. Depending on the biological agent being utilized for research, it may be required to complete additional training courses and/or get approval for a specific protocol from the Institutional Biosafety Committee (IBC) before proceeding with research. For example any study that utilizes human cell lines, even if the cell line is designated at Biosafety Level 1 (BSL1), requires that the researcher complete annually Bloodborne Pathogen Training (https://education.research.utah.edu/class_details.jsp?offeringId=72) prior to initiating experiments. Any work that involves the use of non-exempt recombinant of synthetic nucleic acid molecules research, acute biological toxins, human cell lines classified as BSL2, etc. requires at a minimum

BSL2 training <u>AND</u> approval of protocols and lab audits by the IBC <u>PRIOR</u> to initiating experiments. If you are unclear if your research falls into this latter category, it is important to review the guidelines on the biosafety website at OEHS denoted above. Failure to comply with these rules can lead to major health concerns for individuals and loss of NIH funding at the University of Utah. In addition, it is the responsibility of the PI whose lab will utilize biological materials to register <u>ALL</u> of their work with the IBC through BioRAFT (<u>http://oehs.utah.edu/topics/bioraft</u>). Prof. Bethany Buck-Koehntop (koehntop@chem.utah.edu) has served on the IBC and can help with general inquiries about biosafety designations or protocol forms and procedures.

D. Hazards from Radioactivity

Radioactive nuclei are those that are unstable and achieve a more stable form by emission of radiation. The emitted radiation is characterized as particulate (a, b) or electromagnetic (g). Radiation can pose major health risks, and therefore those working with radioactive materials or X-rays must undertake further training. The Radiological Health Department oversees all aspects of radiological safety at the University of Utah. See their website <u>http://www.rso.utah.edu/</u> for information and radiation safety training.

E. Toxic Chemicals

The chemicals encountered in the laboratory have a broad spectrum of physical, chemical, and toxicological properties and physiological effects. The risks associated with chemicals must be well understood prior to their use in an experiment. The risk of toxic effects is related to both the extent of exposure and the inherent toxicity of a chemical. The extent of exposure is determined by the dose, the duration and frequency of exposure, and the route of exposure. Exposure to even large doses of chemicals with little inherent toxicity, such as phosphate buffer, presents low risk. In contrast, even small quantities of chemicals with high inherent toxicity or corrosivity may cause significant adverse effects. The duration and frequency of exposure are also critical factors in determining whether a chemical will produce harmful effects. A single exposure to some chemicals is sufficient to produce an adverse health effect; for other chemicals repeated exposure is required to produce toxic effects. For most substances, the route of exposure (through the skin, the eyes, the gastrointestinal tract, or the respiratory tract) is also an important consideration in risk assessment. For chemicals that are systemic toxicants, the internal dose to the target organ is a critical factor. Exposure to acute toxicants can be guided by well-defined toxicity parameters based on animal studies and often human exposure from accidental poisoning. The analogous quantitative data needed to make decisions about the neurotoxicity and immunogenicity of various chemicals is often unavailable.

Toxic effects of chemicals occur after single (acute), intermittent (repeated), or long-term repeated (chronic) exposure. An acutely toxic substance causes damage as the result of a single shortduration exposure. Hydrogen cyanide, hydrogen sulfide, and nitrogen dioxide are examples of acute toxins. In contrast, a chronically toxic substance causes damage after repeated or long-duration exposure or causes damage that becomes evident only after a long latency period. Chronic toxins include all carcinogens, reproductive toxins, and certain heavy metals and their compounds. Many chronic toxins are extremely dangerous because of their long latency periods: the cumulative effect of low exposures to such substances may not become apparent for many years. Many chemicals may be hazardous both acutely and chronically depending on exposure level and duration.

All laboratory personnel must understand certain basic principles of toxicology and recognize the major classes of toxic and corrosive chemicals.

Among the thousands of laboratory chemicals, a wide spectrum of doses exists that are required to produce toxic effects and even death. For most chemicals, a threshold dose has been established (by rule or by consensus) below which a chemical is not considered to be harmful to most individuals.

One way to evaluate the acute toxicity (i.e., the toxicity occurring after a single exposure) of laboratory chemicals involves their lethal dose 50 (LD50) or lethal concentration 50 (LC50) value. The LD50 is defined as the amount of a chemical that when ingested, injected, or applied to the skin of a test animal under controlled laboratory conditions kills one-half (50%) of the animals. The LD50 is usually expressed in milligrams or grams per kilogram of body weight.

In evaluating the hazards associated with work with toxic substances, it is important to note that a number of factors influence the response of individuals to exposure to toxic compound. For example, people are rarely exposed to a single biologically active substance. With this point in mind, it is noteworthy that one toxin can influence the effect of a second. Several classic examples are the

dramatically enhanced lung carcinogenicity of combined exposure to asbestos and tobacco smoke. and the potentiating activity of phorbol esters on skin carcinogenesis polycyclic initiated by hydrocarbons. There are insufficient data at present to identify which substances potentiate (or possibly even antagonize) the effects of others, but is important for laboratory workers to be cognizant that such interactions can occur. This point underscores the importance of maintaining good laboratory practices at all times, and with all chemicals



Table 5-5. Percent of population affected plotted versus exposure concentration. Chemical A affects a portion of the population at low-dose, whilst chemical B affects most of the population above a threshold dose.

As a final point, it is also noteworthy that the response of an organism to a toxin typically increases with the dose given, but the relationship is not always a linear one. As one example, some carcinogenic alkylating agents show a biphasic dose-mutation curve resembling a hockey stick pointed upward from left to right. It is now well established that the resistance of many organisms

to mutagenesis by low doses of simple alkylating agents is due in large measure to a genoprotective system; once that system saturates, at the breakpoint in the curve, the organism becomes much more sensitive to the toxin. This example illustrates two points. First, we have systems that protect against low doses of many toxins (not all, but many). But, as a second, cautionary note, it is pointed out that between individuals there are differences in the levels of genoprotection and other toxin defense systems. These differences are in part genetically determined but also are determined in part by the aggregate exposure of the individual to all chemicals within and outside of the laboratory. Accordingly, it is difficult to estimate exactly how sensitive a given person will be on a given day to a given substance. This point urges once again that a cautious approach be taken in handling all chemicals in the workplace.

Types of Toxins

1) <u>Irritants</u>

Irritants are noncorrosive chemicals that cause reversible inflammatory effects (swelling and redness) on living tissue by chemical action at the site of contact. A wide variety of organic and inorganic chemicals are irritants, and consequently, skin and eye contact with all reagent chemicals in the laboratory should be minimized. Examples include formaldehyde, iodine, and benzoyl chloride.

2) <u>Corrosive Substances</u>

Corrosive substances are those that cause destruction of living tissue by chemical action at the site of contact and are solids, liquids, or gases. Corrosive effects occur not only on the skin and eyes but also in the respiratory tract and, in the case of ingestion, in the gastrointestinal tract as well. Corrosive materials are probably the most common toxic substances encountered in the laboratory. Corrosive liquids are especially dangerous because their effect on tissue is rapid. Bromine, sulfuric acid, aqueous sodium hydroxide solution, and hydrogen peroxide are examples of highly corrosive liquids. Corrosive gases are also frequently encountered. Gases such as chlorine, ammonia, chloramine, and nitrogen dioxide damage the lining of the lungs, leading, after a delay of several hours, to the fatal buildup of fluid known as pulmonary edema. Finally, a number of solid chemicals have corrosive effects on living tissue. Examples of common corrosive solids include sodium hydroxide, phosphorus, and phenol. If dust from corrosive solids is inhaled, it causes serious damage to the respiratory tract. There are several major classes of corrosive substances. Strong acids such as nitric, sulfuric, and hydrochloric acid cause serious damage to the skin and eyes. Hydrofluoric acid is particularly dangerous and produces slow-healing painful burns (see Chapter 6, section 6.G.6 in Prudent Practices). Strong bases, such as metal hydroxides and ammonia, are another class of corrosive chemicals. Strong dehydrating agents, such as phosphorus pentoxide and calcium oxide, have a powerful affinity for water and cause serious burns on contact with the skin. Finally, strong oxidizing agents, such as concentrated solutions of hydrogen peroxide, also have serious corrosive effects and should never come into contact with the skin or eyes.

3) Allergens and Sensitizers

A chemical allergy is an adverse reaction by the immune system to a chemical. Such allergic reactions result from previous sensitization to that chemical or a structurally similar chemical. Once sensitization occurs, allergic reactions result from exposure to extremely low doses of the chemical. Some allergic reactions are immediate, occurring within a few minutes after exposure. Anaphylactic shock is a severe immediate allergic reaction that results in death if not treated quickly. Delayed allergic reactions take hours or even days to develop, the skin is the usual site of such delayed reactions, becoming red, swollen, and itchy. Delayed chemical allergy occurs even after the chemical has been removed; contact with poison ivy is a familiar example of an exposure that causes a delayed allergic reaction due to uroshiol. Also, just as people vary widely in their susceptibility to sensitization by environmental allergens such as dust and pollen, individuals also exhibit wide differences sensitivity in their to laboratory chemicals. Because an allergic response is triggered in a sensitized individual by an extremely small quantity of the allergen, it may occur despite personal protection measures that are adequate to protect against the acute effects of chemicals. Laboratory personnel should be alert for signs of allergic responses to chemicals. Examples of chemical substances that cause allergic reactions in some individuals include diazomethane; dicyclohexylcarbodiimide; formaldehyde and phenol derivatives; various isocyanates (e.g., methylene diphenyl diisocyanate (MDI) or toluene diisocyanate (TDI), used in adhesives, elastomers, and coatings); benzylic and allylic halides; metals including nickel, beryllium, platinum, cobalt, tin, and chromium; and acid anhydrides such as acetic anhydrides.

4) Asphyxiants

Asphyxiants are substances that interfere with the transport of an adequate supply of oxygen to vital organs of the body. The brain is the organ most easily affected by oxygen starvation, and exposure to asphyxiants leads to rapid collapse and death. Simple asphyxiants are substances that displace oxygen from the air being breathed to such an extent that adverse effects result. Acetylene, carbon dioxide, argon, helium, ethane, nitrogen, and methane are common asphyxiants. Certain other chemicals have the ability to combine with hemoglobin, thus reducing the capacity of the blood to transport oxygen. Carbon monoxide, hydrogen cyanide, and certain organic and inorganic cyanides are examples of such substances.

5) <u>Neurotoxins</u>

Neurotoxic chemicals induce an adverse effect on the structure or function of the central or peripheral nervous system, which can be permanent or reversible. The detection of neurotoxic effects may require specialized laboratory techniques, but often they are inferred from behavior such as slurred speech and staggered gait. Many neurotoxins are chronically toxic substances with adverse effects that are not immediately apparent. Some chemical neurotoxins that may be found in the laboratory are mercury (inorganic and organic), organophosphate pesticides, carbon disulfide, xylene, tricholoroethylene, and *n*-hexane.

6) <u>Toxins affecting other target organs</u>

Target organs outside the reproductive and neurological systems are also affected by toxic substances in the laboratory. Most of the chlorinated hydrocarbons, benzene, other aromatic hydrocarbons, some metals, carbon monoxide, and cyanides, among others, produce one or more effects in target organs. Such an effect may be the most probable result of exposure to the particular

chemical. Although this chapter does not include specific sections on liver, kidney, lung, or blood toxins, many of the LCSSs mention those effects in the toxicology section.

Particularly Hazardous Substances (PHS)

It is imperative that researchers are familiar with particularly hazardous substances, which, if mishandled, can significantly impact health or even life. These are: substances with a high degree of acute toxicity, select carcinogens, and reproductive toxins. They require additional handling precautions.

1) Compounds with a High Degree of Acute Toxicity

Compounds that have a high degree of acute toxicity comprise the first category of particularly hazardous substances as defined by the OSHA Lab Standard. Acutely toxic agents include certain corrosive compounds, irritants, sensitizers (allergens), hepatotoxins, nephrotoxins, neurotoxins, agents that act on the hematopoietic systems, and agents which damage the lungs, skins, eyes, or mucous membranes (see Part V-A for definitions of these classes of hazardous substances). Substances which have a high degree of acute toxicity are interpreted by OSHA as being substances which "may be fatal or cause damage to target organs as the result of a single exposure or exposures of short duration." "Toxic" and "highly toxic" agents are defined by OSHA regulations as substances with median lethal dose (LD₅₀) values in the ranges discussed in Table 10-1:

	Toxic	Highly Toxic
Oral LD ₅₀ (albino rats)	50-500 mg/kg	<50 mg/kg
Skin Contact LD50 (albino rabbits)	200-1000 mg/kg	<200 mg/kg
Inhalation LC ₅₀ (albino rats)	200-2000 ppm/air	<200 ppm/air

 Table 5-6: Acute Toxicity Hazard Level.

The following lists some of the compounds that may be in current use in chemistry department laboratories and which have a high degree of acute toxicity.

- acrolein
- arsine
- chlorine
- diazomethane
- diborane (gas)
- hydrogen cyanide
- hydrogen fluoride

- methyl fluorosulfonate
- nickel carbonyl
- nitrogen dioxide
- osmium tetroxide
- ozone
- phosgene

• sodium azide

• sodium cyanide (and other cyanide salts)

Note: the above list is not intended to be complete, and it is the responsibility of the researcher (in consultation with their laboratory supervisor) to evaluate each compound involved in their work and to determine whether it is a substance with a high degree of acute toxicity.

2) <u>Select Carcinogens</u>

Certain potent carcinogens are classified as "select carcinogens" and treated as PHS's. A select carcinogen is defined in the OSHA Lab Standard as a substance that meets one of the following criteria:

- It is regulated by OSHA as a carcinogen,
- It is listed as "known to be a carcinogen" in the latest Annual Report on Carcinogens published by the National Toxicology Program (NTP),
- It is listed under Group 1 ("carcinogenic to humans") by the International Agency for Research on Cancer (IARC), or
- It is listed under IARC Group 2A or 2B, ("probably carcinogenic to humans") or under the category "reasonably anticipated to be a carcinogen" by the NTP, and causes statistically significant tumor incidence in experimental animals in accordance with any of the following criteria: (i) after inhalation exposure of 6-7 hours per day, 5 days per week, for a significant portion of a lifetime to dosages of less than 10 mg/m3; (ii) after repeated skin application of less than 300 mg/kg of body weight per week; or (iii) after oral dosages of less than 50 mg/kg of body weight per day.

The following lists the substances meeting criteria given above:

- 2-acetylaminofluorene
- acrylamide
- acrylonitrile
- 4-aminobiphenyl
- arsenic and certain arsenic compounds
- asbestos
- azathioprine
- benzene
- benzidine
- bis(chloromethyl) ether
- 1,4-butanediol dimethylsulfonate (myleran)
- chlorambucil
- chloromethyl methyl ether
- chromium and certain chromium compounds

- coal-tar pitches
- coal tars
- conjugated estrogens
- cyclophosphamide
- 1,2-dibromo-3-chloropropane
- 3,3'-dichlorobenzidine (and its salts)
- diethylstilbestrol
- dimethylaminoazobenzene
- dimethyl sulfate
- ethylene dibromide
- ethylene oxide
- ethylenimine
- formaldehyde
- hexamtehylphosphoramide
- hydrazine
- melphalan

- 4,4'-methylene-bis(2chloroaniline)
- mustard gas
- N,N'-bis(2-chloroethyl)-2naphthylamine
- (chlornaphazine)
- α-naphthylamine
- β-naphthylamine
- nickel carbonyl

- 4-nitrobiphenyl
- N-nitrosodimethylamine
- β-propiolactone
- thorium dioxide
- treosulphan
- vinyl chloride

Note: the above list is not intended to be complete, and it is the responsibility of the researcher (in consultation with their laboratory supervisor) to evaluate each compound involved in their work and to determine whether it should be handled as a select carcinogen.

A list of carcinogenic compounds can be found at the CDC website: http://www.cdc.gov/niosh/topics/cancer/npotocca.html.

3) <u>Reproductive Toxins</u>

Reproductive toxins act during pregnancy and cause adverse effects on the fetus; these effects include embryolethality (death of the fertilized egg, embryo or fetus), malformations (teratogenic effects), and postnatal functional defects. Examples of embryotoxins include thalidomide and certain antibiotics such as tetracycline. Women of childbearing potential should note that embryotoxins have the greatest impact during the first trimester of pregnancy. Because a woman often does not know that she is pregnant during this period of high susceptibility, special caution is advised when working with all chemicals, especially those rapidly absorbed through the skin (e.g., formamide).

Information on reproductive toxins can be obtained from Material Safety Data Sheets, by contacting OEHS, and by consulting the Catalog of Teratogenic Agents, Sixth Edition; Shepard, T. H.; Johns Hopkins University Press, Baltimore, 1989. Also see Beyler, R. E. and Meyers, V. K. J. Chem. Ed. 1982, 59, 759-763 for a discussion of "What Every Chemist Should Know About Teratogens." The following Table lists some common materials that are suspected to be reproductive toxins; in some laboratories it will be appropriate to handle these compounds as particularly hazardous substances.

The following lists the substances meeting criteria given above:

- arsenic and certain arsenic compounds
- lead compounds
- benzene
- mercury compounds
- cadmium and certain cadmium compounds

- toluene
- carbon disulfide
- vinyl chloride
- ethylene glycol monomethyl and ethyl ethers
- xylene
- ethylene oxide

Note: The above list is not intended to be complete, and it is the responsibility of the researcher (in consultation with their laboratory supervisor) to evaluate each compound involved in their work and to determine whether it should be handled as a reproductive toxin.

F. <u>Physical Hazards</u>

These hazards include compressed gases, nonflammable cryogenics, high-pressure systems, vacuum work, UV-vis-near IR radiation, electrical hazards, magnetic fields, sharp edges, and ergonomic hazards.

Compressed Gases

Compressed gases expose laboratory personnel to both chemical and physical hazards. If the gas is flammable, flash points lower than room temperature compounded by rapid diffusion throughout the laboratory present the danger of fire or explosion. Additional hazards arise from the reactivity and toxicity of the gas. Asphyxiation can be caused by high concentrations of even inert gases such as nitrogen. An additional risk of simple asphyxiants is head injury from falls due to rapid loss of oxygen to the brain. Death can also occur if oxygen levels remain too low to sustain life. Finally, the large amount of potential energy resulting from the compression of the gas makes a highly compressed gas cylinder a potential rocket or fragmentation bomb.

To minimize the risks of gas mixing/release, all gas cylinders and accessories are labeled with a CGA number (Figure 5-7), which is specific to each gas (See Appendix G). To minimize accidental equipment mismatch/mixing, flammable gases are reverse-thread.



All gas cylinders must be double-chained to the wall, and when not in use, stored with a cap and no regulator. Proper training is required for use of compressed gases.

Nonflammable Cryogens

Cryogenic liquids are fluids with boiling points less than -73°C (-100°F). They are also characterized by a high volume-expansion ratio in the liquid to gas phase. Some physical properties of three reference cryogenic liquids are outlined in Table 11-2.

Identity	Boiling Point	Vapor Pressure (at -196°C)	Volume-Expansion Ratio (at 1 atm, 20°C)
Nitrogen (<i>l</i>)	-195.8°C	730 mm Hg	1:696
Oxygen (l)	-182.9°C	150 mm Hg	1:861
Carbon Dioxide (<i>l</i>)	-78.5°C	1.33 × 10 ⁻⁸ mm Hg	1:553

Table 5-8: Common Characteristics of Cryogenic Liquids.

Hazards to consider when working with cryogenic liquids include cold burns/frost bite from liquids in contact with skin or eyes. Appropriate PPE includes safety goggles, lab coats, closed toe shoes, and clothing that covers arms and legs. Insulated gloves which are easily removed can be worn, but are not recommended due to the high risk of cold burns (with liquid nitrogen). Likewise latex or nitrile gloves can capture splashes of cryogens and hold them close to the skin causing burns as the liquid expands as it warms. Additionally, inadequate ventilation poses asphyxiation hazards as oxygen-containing air is displaced. Do not use cryogenic fluids in small, closed rooms or rooms with inadequate ventilation. Embrittlement of structural materials is also a hazard of cryogenics, as is pressure buildup.

Explosion hazards should also be considered, as many cryogenic fluids can condense oxygen from the air to generate liquid oxygen. Liquid oxygen is flammable and explosive; it is characterized by a light, clear blue color. When in combination with organic compounds, the explosive nature of liquid oxygen is exacerbated.

Work and transportation of cryogenics requires additional training.

High-Pressure Reactions

Experiments that generate high pressures, are carried out at elevated pressures, or are run in supercritical fluids, can lead to explosion from equipment failure. Additional safety training is required to carry out such work.

Vacuum Work

Precaution must be taken when working at sub-ambient pressures. The main danger is injury from glass breakage, and release of chemicals, which may catch fire, explode, or be toxic. Additionally, most vacuum lines require cold traps, which pose additional hazards. Additional training is required for vacuum line work that makes use of liquid nitrogen cold traps.

UV, visible, and near-IR Radiation

UV, visible, and near-IR radiation from lamps and lasers can produce many hazards. UV lamps used in biosafety cabinets and light boxes can cause serious skin and corneal burns. Powerful arc lamps can cause eye damage and blindness within seconds. Some compounds are explosively photosensitive.

Incorrect use of lasers can pose hazard to the eyes, and is also a potential fire hazard. Depending on the type of laser, additional hazards can include: mutagenic, carcinogenic, or otherwise toxic laser dyes and solvents; flammable solvents; UV or visible radiation from the pump lamps; and electric shock from the lamp power supplies.

Additional training is required for use of UV, visible, and near-IR radiation.

<u>Electrical Hazards</u>

Electrocution hazards of electrically powered instruments, tools, and other equipment are essentially eliminated by safety features built into the systems. However, the possibility of serious injury or death by electrocution is very real if attention is not paid to engineering, maintenance, and personal work practices. It is advised that researchers check the integrity of their electrical equipment. Chemicals in the lab can lead to eroded insulation on wires. These should be repaired immediately, particularly if they are located in near proximity to water (or cold environments). Equipment malfunctions can also lead to fires. If equipment results in tripping of a circuit, lab personnel should not reset the circuit breaker but instead have the electric shop check the integrity of the electronic equipment. *Repair and modification of electrical equipment should be done by the electronics shop*.

All lab personnel should know the location of the lab power shut off. This is usually located by a door, and is a large red switch. Personnel should also be aware of hazards that may arise after power outages when power returns to the lab. Each lab should have a plan of action for such a scenario.

Magnetic Fields

Many instruments, such as NMR spectrometers, have magnetic fields on the order of 14,000 to 235,000 G. The magnitude of these static magnetic fields drop off rapidly with distance. Also, many instruments have internal shielding, which reduces the strength of the field outside the instrument. Strong attraction occurs when the magnetic field is greater than 50 to 100 G and increases as the separation is reduced. Those with metal implants should be cautious of the distance they maintain with these instruments. These instruments should be marked with the "safe" distance. If in doubt, contact the manufacturer of your medical implant.

<u>Sharp Edges</u>

A common lab injury has to do with cuts and punctures from broken glasses, needles, and other sharp objects. To minimize such injuries, personnel should take the following precautions:

- Use correct procedures (for instance, do not over-pressurize a glass vessel)
- Check glassware for chips and cracks. These render the glassware prone to breakage, but can readily be fixed by the glassblower.
- Dispose of broken glass in glass disposal, not the regular trash.
- When using razors, ensure that the edge is sharp, and keep hands out of the line of the cut. Also stand off-line from the direction of the cut.

Ergonomic Hazards

Personnel should not ignore ergonomic hazards that come with lab work. Repetitive motion and awkward posture due to instrument positioning can lead to strains and over-use injuries. More information on ergonomics can be found here: <u>http://www.cdc.gov/niosh/topics/ergonomics/</u>. A checklist that helps evaluate ergonomic hazards in the lab can be found here: <u>http://www.ehs.ucr.edu/ehsacademy/presentations/ergonomicslaboratorychecklist.pdf</u>.

VI. Protecting Yourself From Chemicals

A. <u>Routes of Exposure</u>

Exposure to chemicals in the laboratory occurs by several routes: (1) inhalation, (2) contact with skin or eyes, (3) ingestion, and (4) injection. Important features of these different pathways are detailed below.

<u>Inhalation</u>

Toxic materials that enter the body via inhalation include gases, the vapors of volatile liquids, mists and sprays of both volatile and nonvolatile liquid substances, and solid chemicals in the form of particles, fibers, and dusts. Inhalation of toxic gases and vapors produces poisoning by absorption through the mucous membranes of the mouth, throat, and lungs and also damages these tissues seriously by local action. Inhaled gases and vapors pass into the capillaries of the lungs and are carried into the circulatory system, where absorption is extremely rapid. Because of the large surface area of the lungs in humans (approximately 75 m²), they are the main site for absorption of many toxic materials.

Contact with skin or eyes

Chemical contact with the skin is a frequent mode of injury in the laboratory. Many chemicals injure the skin directly by causing skin irritation and allergic skin reactions. Corrosive chemicals

cause severe burns. In addition to causing local toxic effects, many chemicals are absorbed through the skin in sufficient quantity to produce systemic toxicity. The main avenues by which chemicals enter the body through the skin are the hair follicles, sebaceous glands, sweat glands, and cuts or abrasions of the outer layer. Absorption of chemicals through the skin depends on a number of factors, including chemical concentration, chemical reactivity, and the solubility of the chemical in fat and water. Absorption is also dependent on the condition of the skin, the part of the body exposed, and duration of contact. Differences in skin structure affect the degree to which chemicals are absorbed. In general, toxicants cross membranes and thin skin (e.g., scrotum) much more easily than thick skin (e.g., palms). Although an acid burn on the skin is felt immediately, an alkaline burn takes time to be felt and its damage goes deeper than the acid. When skin is damaged, penetration of chemicals increases. Acids and alkalis injure the skin and increase its permeability. Burns and skin diseases are the most common examples of skin damage that increase penetration. Also, hydrated skin absorbs chemicals better than dehydrated skin. Some chemicals such as dimethyl sulfoxide actually increase the penetration of other chemicals through the skin by increasing its permeability.

Contact of chemicals with the eyes is of particular concern because the eyes are sensitive to irritants. Few substances are innocuous in contact with the eyes; most are painful and irritating, and a considerable number are capable of causing burns and loss of vision. Alkaline materials, phenols, and acids are particularly corrosive and can cause permanent loss of vision. Because the eyes contain many blood vessels, they also are a route for the rapid absorption of many chemicals.

<u>Ingestion</u>

Many of the chemicals used in the laboratory are extremely hazardous if they enter the mouth and are swallowed. The gastrointestinal tract, which consists of the mouth, esophagus, stomach, and small and large intestines, can be thought of as a tube of variable diameter (approximately 5 m long) with a large surface area (approximately 200 m²) for absorption. Toxicants that enter the gastrointestinal tract must be absorbed into the blood to produce a systemic injury, although some chemicals are caustic or irritating to the gastrointestinal tract tissue itself. Absorption of toxicants takes place along the entire gastrointestinal tract, even in the mouth, and depends on many factors, including the physical properties of the chemical and the speed at which it dissolves. Absorption increases with surface area, permeability, and residence time in various segments of the tract. Some chemicals increase intestinal permeability and thus increase the rate of absorption. More chemical will be absorbed if the chemical remains in the intestine for a long time. If a chemical is in a relatively insoluble solid form, it will have limited contact with gastrointestinal tissue, and its rate of absorption will be low. If it is an organic acid or base, it will be absorbed in that part of the gastrointestinal tract where it is most fat soluble. Fat-soluble chemicals are absorbed more rapidly and extensively than water-soluble chemicals.

Injection

Exposure to toxic chemicals by injection does not occur frequently in the laboratory, but it occurs inadvertently through mechanical injury from sharp objects such as glass or metal contaminated with chemicals or syringes used for handling chemicals. The intravenous route of administration is especially dangerous because it introduces the toxicant directly into the

bloodstream, eliminating the process of absorption. Non-laboratory personnel, such as custodial workers or waste handlers, must be protected from exposure by placing sharp objects in special sharps containers and not ordinary scrap baskets. Hypodermic needles with blunt ends are available for laboratory use to minimize puncture risks.

VII. Chemical Storage, Inventory, Transport, and Waste

A. Chemical Storage

Most chemicals will be stored in vented, fire-resistant cabinets, either free standing or under hoods. Additional storage on shelves and fridges may be required. All chemicals must be stored in a secondary container (for example, large plastic bins that have sufficient volume to contain spills). In most instances, several chemicals that are compatible will be stored together in a single secondary bin. The chemicals should be organized in a systematic manner that is mirrored in the chemical inventory. Details of how chemicals are organized are at the discretion of each research group, but chemicals MUST be segregated by compatibility. Additionally, it is recommended that each cabinet/storage area be labeled on the outside with the storage group and/or chemicals inside.



The segregation shown in Figure 6-1 is suggested though may not be practical due to space and quantity. Under no circumstances should incompatible chemicals be stored in the same cabinet together. An alternative storage system that works well for existing storage systems is to have a list of incompatible chemicals on each storage unit, with chemicals inside highlighted. Researchers who add chemicals are responsible for checking the compatibility of the new chemical with what is stored, and if needed, highlighting a new chemical type. A partial list of chemical incompatibilities is found as Appendix F.

Flammables must be stored in flame-retardant cabinets or fridges. Chemicals that are explosive hazards should be stored in an explosion-proof fridge or cabinet. When not in use, gas cylinders must be double-chained to the wall, stored with the cap on and regulator off. Peroxide forming chemicals should be stored in the dark.

<u>Labeling</u>

All chemicals must be labeled and placed in secondary containers in cabinets. The outside cabinets should also be labeled (see above).

Chemicals should be labeled with the date of arrival and the date opened.

It is highly advised that peroxide-forming chemicals, those that require further training by the group, and any additional precautions have an additional colored label on the cap. For instance, all peroxide forming chemicals may be labeled with pink lab tape on the caps, warning lab personnel of the potential hazard, and allowing for easy identification of these chemicals that must be periodically tested for peroxides. Chemicals that can only be used after additional group training may be labeled with green tape, warning lab personnel that they can only use the chemicals after additional training. It is at the discrepancy of research groups whether they adopt this additional system, and hoe detailed/elaborate it is. If adapted, a key for the color-coding must be present on the outside of all chemical storage units.

B. Chemical Inventory

The department of chemistry uses the LabSuit inventory system (<u>www.labsuit.com</u>). Lab members can view and edit their group's inventory. New lab members should contact their group safety officer to gain access. Additionally, the group may choose to share their inventory with members of the department by joining the Labs Around Me Community. The inventory can be downloaded as an excel spreadsheet and printed in case of a power outage or stored on the desktop of a group computer in case the internet goes down.

It is the responsibility of each group to keep the inventory up-to-date with the name and CAS number for all chemicals, location (building and room number), quantity (for example 3 - 250 mL bottles), physical state (solid, liquid, gas), and date of purchase or receipt. The inventory should be reviewed and updated at least annually.

C. Transportation of Chemicals

All chemicals must be transported in appropriate secondary containers. This includes picking up chemicals from the stockroom, and taking chemicals from one part of the building to others.

Under no circumstances should personnel ride on the elevator with liquid nitrogen. This is because in case of a spill and/or elevator failure, asphyxiation is a real danger. Liquid nitrogen (in any quantity) should be transported using the stairs. If an elevator is required, it is the responsibility of the researcher transporting the liquid nitrogen to ensure that no one gets on the elevator with the liquid nitrogen. This is readily done by posting personnel at each floor between the originating/destination floor. See signs in elevators for further information.

D. <u>Chemical Waste</u>
The University of Utah has adopted the University Hazardous Waste Rule (aka subpart K). This rule allow for modified handling of unwanted hazardous materials to facilitate laboratory scale operations. All containers must be labeled "Unwanted Materials" not "waste."

The best strategy for managing laboratory waste aims to maximize safety and minimize environmental impact, and considers these objectives from the time of purchase.

The initial responsibility for proper handling of unwanted materials rests with trained laboratory personnel. These individuals are in the best position to know the chemical and physical properties of the materials they have used or synthesized. They are responsible for evaluating hazards, providing information necessary to make an accurate waste determination, and assisting in the evaluation of appropriate strategies for management, minimization, and disposal.

The overriding principle governing the prudent handling of laboratory waste is that *no activity* should begin unless a plan for the disposal of nonhazardous and hazardous waste has been formulated.

There are four tiers to waste management to reduce its environmental impact: pollution prevention and source reduction; reuse or redistribution of unwanted, surplus materials; treatment, reclamation, and recycling of materials within the waste; and disposal through incineration, treatment, or land burial. The first tier of this strategic hierarchy incorporates the principles of green chemistry: pollution prevention and source reduction. Clearly, the best approach to laboratory waste is preventing its generation. Examples include reducing the scale of laboratory operations, reducing the formation of waste during laboratory operations, and substituting nonhazardous or less hazardous chemicals in chemical procedures.

The second strategic tier is to reuse unwanted material, redistribute surplus chemicals, and reduce hazards. Practices that implement this strategy include purchasing only what is needed, keeping chemical inventories to prevent the purchase of duplicates, and reusing excess materials. Sanitary sewer disposal of chemicals is not allowed. Occupational and environmental health and safety (OEHS) staff determine the point at which the chemical becomes regulated as a waste and ensures that requirements are met. The determination of whether a waste is regulated as hazardous is made by OEHS.

Collection and Storage (including how to fill out tag, get trained with OEHS)

- 1) Go to <u>https://OEHS.utah.edu/</u>
- Go to Resource Center then Forms/Checklists. Scroll down to <u>Lab Management</u> <u>System – Account Request / Password Reminder</u>. Click it, and follow the instructions to receive lab management system login information.
- 3) Once you receive your loigin information go to the Lab Management System (<u>http://oehs.utah.edu/topics/lab-management-system</u> or find under Topics on the OEHS website). Feel free to change your password from the automatically generated one from the email.
- 4) Once logged in, click "Unwanted Materials Pickup."
- 5) On the next screen click the "Add Request" button

- 6) Enter the building and room number into the location box and fill out the rest of the form
- 7) On the next page, you need to select the type of waste, containers, etc. and fill out the form. You need a new form for each separate type of waste container.
 - a. Organic wastes are represented by a representative example of the majority of the halogenated or non-halogenated waste in the container in percentages. (ex. 40% acetone, 10% DCM, 10% ether, 10% hexanes, 10% Ethyl Acetate, 5% toluene, 5% THF, 5% methanol, 5% pentane)
 - b. If there are special waste concerns with a particular container (ex. Explosive compounds, etc.) be sure to make a separate form for that container.
 - c. Used vacuum pump oil is requested as "100% used pump oil"
 - d. Sharps waste is listed under biological waste
- 8) Once you have entered all of the lab's waste information and requested an appropriate number of replacement disposal containers, submit the request.
- 9) On the next screen, you must download the pdf of the reports and print the tag for each separate container. The pdf has a huge tag, so it may be easier to snapshot and copy it in adobe and paste and then shrink it on a word document, considering the system only generates one tag for each different type of waste.
- 10) Tape these tags to the appropriate waste containers in the appropriate room and wait for OEHS to come pick them up and drop off new containers.

VIII. Emergency Preparedness

A. Fire Extinguishers, Fire Blankets, Safety Showers, and Eyewash Facilities

Fire Extinguishers

The University of Utah does not require that personnel extinguish fires that occur in their area, though under certain circumstances, researchers who have been trained to use extinguishers can put out fires. Personnel are not allowed to use extinguishers unless they have been properly trained to do so. Contact the University Fire Marshal at 801-581-6590 for information on the next extinguisher training session.

Fire extinguishers are located in the hallways (A/B/C). All extinguishers are electronically monitored. Any time an extinguisher is used, contact Facilities Maintenance Fire Prevention Shop at 801-581-7221 so that it can be inspected and recharged.

There are various types of fires; those pertinent to the chemistry department are:

A (for ash): fires that are comprised of solid combustibles, including paper/trash can fires

B (for barrel): flammable liquids/gases, including solvents

C (for current): electrical fires

D (for dynamite): metal fires (note, requires a different extinguisher!)

There are several types of extinguishers that can be used to put out different types of fires. All extinguishers are labeled with the type of fire they can put out. Details on those found within the Department of Chemistry are given below.

Carbon Dioxide extinguishers are effective against Class B and C fires (burning liquids and electrical fires). They are less effective for type A fires (burning paper), and should not be used for type D fires (burning metals and pyrophoric organometallic/main group reagents). These extinguishers are clean, leaving no chemical residue behind.

Dry Powder extinguishers are effective against Class A, B and C and should not be used for type D fires. They contain sodium bicarbonate and leave a powder behind.

Met-L-X extinguishers are effective for class D fires. These are available upon request from OEHS.

Sand can be used to smother any type of fire, and is particularly useful for putting out small type D fires. Note, smothering type D fires does not quench the pyrophoric material, which must still be properly quenched (see Appendix F).

To put out a fire, using an extinguisher, remember PASS: Pull, Aim, Squeeze, Sweep. A/B/C extinguishers should be aimed in front of the flames, whilst D extinguishers should be aimed on top of the flames.

<u>Fire Blankets</u>

Fire blankets are located in certain labs, but are not recommended as a first aid measure; smothering a person on fire can result in more severe burns. If a person is on fire, it is recommended that they be moved to the emergency shower immediately and/or for the burning clothes removed.

Emergency Showers and Eyewash Stations

Emergency showers are located within all labs, and should be checked periodically by the group safety officer to ensure proper function. Issues should be reported to Facility Operations at 801-581-7221. Modesty should never be an issue in an emergency, and all researchers should devise a plan that they have discussed with their lab peers/PI on what they will do if they must strip and use the safety shower (clothes on fire, major chemical exposure to skin, etc.). For instance, it may be that all those of the opposite gender leave and get help, while those of the same gender use the fire blanket as a makeshift curtain. Personnel are encouraged to keep a spare change of clothes in the office for these instances.

Eyewash stations are located near all safety showers, and should be checked weekly by the group safety officer to ensure proper function and to flush out any bacteria that grow in stagnant water. Issues should be reported to OEHS. Note, eyewash stations will not necessarily flush out

contact lenses, so it is up to each researcher to notify the rest of the research group that he/she wears contact lenses. This information can readily be stored as part of the emergency contact information.

B. General Emergency Preparation

- Every group should have a safety officer/fire warden, whose responsibility is to familiarize lab members with emergency and evacuation procedures, carry out monthly visual inspections of the safety equipment, and conduct "sweeps" of the working area during evacuations. They also keep track of emergency contact info.
- All lab members MUST have cell phone #s of every group member programmed in their cell phones. Note: University policy is that all labs must have functioning land line telephone in, or close to, the lab.
- Every group member should be trained on using the safety equipment in the lab as part of the initial safety training to work in the group.
- For work with dangerous chemicals or procedures, researchers must be trained by appropriate personnel and checked out by the safety officer/PI. This must be documented within the group.
- Every lab should post a map of where safety equipment is on lab doors. This includes spill kits, fire extinguishers, first aid kits, safety showers, eye wash stations, and fire blankets.
- Every lab should have Campus Emergency Flip Chart from OEHS. Updated flipcharts can be requested by contacting our Department of Chemistry representative, Matt Lundquist at <u>matt.lundquist@oehs.utah.edu</u>.
- Under no circumstances should exits be blocked (in the lab or hallways).
- Each lab should have an up to date hazard warning sign posted, with numbers of who to contact in case of an emergency. To request new signage go to http://oehs.utah.edu/resource-center/forms/hazard-warning-signage-questionnaire
- Additionally, each lab should have up-to-date emergency contact information. It is highly recommended that this information be shared with neighboring research groups. These lists should be kept in an envelope taped to the door so that they are easily accessible when evacuating.
- Always be prepared with what you are doing in the lab- know the hazards, minimize your exposure to chemicals, do not under-estimate the risks, and be prepared for accidents.

- Hood sashes should list what is going on in the hood (reactions), with hazards and what to do in case of an emergency, and/or notebook name/number/page. Hoods should also have a phone number for who to call in case of an emergency. Alternatively, an open notebook page detailing this information near the hood is also appropriate.
- Do not work alone- if you must, have someone check in on you or call you periodically and NEVER use chemicals that have increased hazards, such as pyrophorics, etc.

C. Emergency Procedures

- To summon emergency police, fire, or ambulance, call campus police at 911 or 9-911 from a campus phone. Report the location of the emergency (building and room), and be as specific as possible about nature of emergency and what is needed. If you are unsure, you may get a "full force" response.
- You can call OEHS for advice and counsel. OEHS personnel are available 24/7 during normal business hours by calling 801-581-6590 and after hours by calling UUPD dispatch at 801-585-2677 and asking them to page OEHS Occ Hygiene on-call.
- Notify other workers in the area of the nature of the emergency, if necessary, activate the fire alarm to order evacuation of the building.
- If a coworker has ingested a toxic substance, follow the first aid information on the SDS and seek medical attention.
- If a coworker is bleeding profusely, elevate the wound above the level of the heart and apply pressure with a clean cloth or your hand. Seek immediate medical assistance. Note if there is glass shrapnel in wound, do not remove.

Do not touch a person in contact with a live electrical circuit- disconnect the power first.

D. <u>Evacuation</u>

Departmental Evacuation Plan

Follow the departmental guideline for evacuation and meeting points.

Assessing the lab prior to evacuation

During an evacuation, personnel should assume that they will not return for several hours. Therefore, it is the responsibility of lab personnel to ensure that the lab is safe. This may require instruments be turned off, reactions placed under inert atmospheres, chemicals be put away, and reactions/procedures stopped (for example, distillations) as long as it is safe to do so.

E. Power Outages

In the case of power outages, it is advised that personnel secure the lab and evacuate. Researchers should ensure that chemicals are properly stored, reactions/equipment in a stable state, etc. It may be advised to unplug equipment if power surges are a concern.

F. <u>Treatment of Injured or Contaminated Persons</u>

- Ingestion: Call emergency personnel (911). Do not encourage vomiting except under the advice of a physician. Call the Poison Control Center (800-222-1222) immediately and consult the SDS for the appropriate action. Save all chemical containers and a small amount of vomitus, if possible, for analysis. Stay with the victim until emergency medical assistance arrives. Send a copy of the MSDS with the victim.
- If a chemical gets in the eye of a victim, flush for a minimum of 15 minutes with eyewash station. Note that soft contact lenses will not necessarily be flushed out, so the victim (or you!) may have to remove contact lenses (hard or soft). Hold the individual's eyelids away from the eyeball, and instruct him or her to move the eye up and down and sideways to wash thoroughly behind the eyelids. Follow first aid by prompt treatment by medical personnel or an ophthalmologist who is acquainted with chemical injuries. Send a copy of the MSDS with the victim. Note: these eye wash stations should be flushed weekly to ensure proper function.
- For spills covering small amounts of skin: immediately flush with water for at least 15 minutes. If there is no visible burn, wash with water and soap, and remove any jewelry / clothing in the area. Check the SDS to see if any delayed effects should be expected (example). It is advised to seek medical attention for even minor chemical burns.
- For spills on clothes: The emergency responder should wear appropriate PPE during emergency treatment to avoid exposure. Do not attempt to wipe the clothes. To avoid contamination of the victim's eyes, do not remove the victim's eye protection before emergency treatment. Quickly remove all contaminated clothing, shoes, and jewelry while using the safety shower. Seconds count; do not waste time or limit the showered body areas because of modesty. Take care not to spread the chemical on the skin or, especially, in the eyes. Cut off garments such as pullover shirts or sweaters to prevent spreading the contamination, especially to the eyes. Immediately flood the affected body area with water for at least 15 minutes. Resume if pain returns. Get medical attention as soon as possible.

The affected person should be escorted and should not travel alone. Send a copy of the SDS with the victim. If the institution's SDS is digital, hardcopies of the relevant information should be provided to responders. If the SDS is not immediately available, it is vitally important that the person in charge convey the name of the chemical to the medical personnel.

• In the event that use of a shower or eyewash is warranted we recommend that someone call 911 immediately – that way medical personnel should be on scene by the time the 15 minute flush is done.

Additional information on handling emergency situations is outlined in Prudent Practices page 117.

G. Spill Containment and Clean-Up

<u>Pre-planning</u>

Personnel should be familiar with the properties (physical, chemical, and toxicological) of hazardous substances before working with them. Research groups should develop SOPs and contingency plans on what to will do with the accidental release of chemicals that pose additional risks. Researchers should ensure that they have the necessary safety equipment, protective apparel, and spill control materials readily available.

- Every research group that works with hazardous substances should have a group spill kit that is tailored to deal with the potential hazards found in the lab. Spill kits can be purchased from OEHS (Make sure the lab has a spill kit that contains appropriate chemicals/supplies to handle spills. Spill kits are available for purchase from OEHS (<u>http://oehs.utah.edu/resource-center/forms/spill-kit-order-form</u>). The kits might include:
 - Spill pillows and pads: used for absorbing solvent and corrosives (not HF). Note: yellow → corrosives, grey → universal (available in the stockroom)
 - Inert absorbents such as vermiculite and sand
 - Neutralizing agents: sodium bicarbonate (acids), and citric acid or sodium bisulfate (for alkaline spills)
 - Equipment such as large plastic scoops, brooms, pails, bags, dustpans, mops, buckets, etc.
 - Sulfur (for mercury) (NOTE: OEHS sells Hg spill kits)

<u>Major Spills</u>

Major hazardous material spills should be reported to OEHS immediately (801-581-6590) to obtain professional assistance and support to control and clean up the spilled material. These spills are defined as those that pose a significant threat to safety, health, or the environment. They often

involve a highly toxic material or materials spilled in large quantities or that pose significant fire hazards, cannot be recovered before release into the environment, or involve a spill in a public area such as a hallway. After reporting, personnel should stand by at a safe distance to guide responders and spill cleanup experts to the spill area, and open all hood sashes. Prevent other personnel from entering the area.

<u>Minor Spills</u>

Minor spills are spills of material that is not highly toxic, is not spilled in large quantity, does not present a significant fire hazard, can be recovered before it is released into the environment, and is not in a public area such as a hallway. Minor spills can usually be cleaned up by 1-2 people using basic spill kit materials. (Note custodians are not allowed to clean-up such spills). OEHS can offer technical advice, but is not responsible for spill cleanup. The Laboratory Chemical Safety Sheets and Prudent Practices gives advice on how to clean up a variety of spills. If large quantities of solvent are on the lab floor, shut off power to lab (to avoid sparks with electrical equipment/major fires) prior to clean up. Also, open all hoods in the lab to help remove fumes.

General Procedure to Clean Up Spills

1. Treat Injured and Contaminated Personnel first.

If an individual is injured/contaminated with a hazardous substance, treating them takes precedence over spill control measures – see section B.6 above on Treatment of injured or contaminated persons.

2. Notify Personnel in the area

Alert other co-workers in the lab of the accident and the nature of the chemicals involved. In the event of the release of highly toxic gases or volatile material, evacuate the lab and post personal at each entrance to prevent other workers from entering the contaminated area. In the case of a major spill, it may be appropriate to activate the fire alarm to evacuate the building.

3. Clean up spills promptly

How you clean up the spill will depend on the size, location, and what it is. Some general guidelines for cleaning up minor spills are given below. For more information, see "Tested Methods for the Handling of Small-Scale Spills,: M.-A. Armour, D. Ashick, and J. Konrad, *Chemical Health and Safety* **1999**, 6, Jan-Feb, 24-27. This article is available on the Safety Canvas site.

• Materials of low flammability that are not volatile or have low toxicity (this includes inorganic acids, and caustic bases):

For clean-up, wear appropriate protective apparel. Neutralize the spills with solutions of neutralizing agent (to avoid excessive fumes). Absorb the material, and dispose of waste accordingly.

• Flammable solvents:

Fast action is required. This category includes pentanes, ethers, etc. Immediately alert other workers in the laboratory, extinguish all flames, and turn off any spark-producing equipment (Note, should not have electrical equipment on ground, and/or outlets/extension cords near ground). In some instances, you may want to turn off power to lab (main switch is next to doors in NHEB). As quickly as possible, the spilled solvent should be soaked up with spill pads/pillows, which should be sealed in containers and disposed of accordingly.

• Highly Toxic Substances:

Do not attempt clean-up by yourself. Notify other personnel of spill, evacuate the area, and contact OEHS to obtain assistance in evaluating the hazards involved.

H. Leaking Gas Cylinders

- Occasionally a gas cylinder or one of its components will develop a leak (usually at the valve threads, safety device, valve stem, and valve outlet). If you suspect a leak, do not use a flame for detection; use soapy water. If the leak cannot be remedied by tightening, contact OEHS.
- Note, when using gas cylinders, it is critical that you use regulators with the correct CGA number (no exceptions!) to avoid unnecessary leaks, injury, damage to tank, and \$\$. See Appendix G for a table of CGA Connection numbers.
- When attaching a regulator, do not use Teflon tape.
- Note, gases that pose toxic hazards (such as CO) should have detectors attached to the tank (\$20 at Home Depot for CO detector).
- For minor leaks, do the following:
 - Flammable, inert, or oxidizing gases: Move the cylinder to an isolated area (away from combustible material if the gas is flammable of an oxidant) and post signed describing the hazards/state warnings. If possible, move the cylinder into a fume hood. Call OEHS for assistance if needed (they have a cylinder leak response kit that can handle most leaks).
 - Corrosive gases: May increase the size of the leak as they are released and some are also oxidants or flammable. Move the cylinder into an isolated, well-ventilated area and use suitable means to direct the gas into an appropriate chemical neutralizer. Post signs that state the hazards and warnings. Note: for these gases,

always use a regulator with a cross-purge assembly (for an inert gas) to minimize the risks of developing leaks in the regulator. Also, promptly flush out/remove regulator (esp. if without a cross-purge assembly) from tank, to avoid permanently having regulator on tank (example). Corrosives regulators are very \$\$\$\$!

- o Toxic gases: Follow the same procedure as for corrosive gases.
- If the nature of the leaking gas or the size of the leak constitutes a more serious hazard, evacuate personal and call campus police from a distance to obtain emergency assistance (pull the fire alarm if a MAJOR leak).

I. <u>Fires</u>

Researchers should be familiar with the types of fires: A, B, C, D (see section 8). Only researchers who have completed fire extinguisher training should attempt to use a fire extinguisher. If a researcher is not trained or is not comfortable putting out the fire, the fire alarm should be pulled. Fires that typically can be put out by researchers include:

- o Fires from quenching small amounts of pyrophoric reagents
- Trash can fire (move to an empty hood before extinguishing)
- Fires in hoods (if large or there are many flammables present, lower sash and call for help).

Contact the Fire Marshall (801-585-9122) to set up a fire extinguisher training.

J. Accidents and Near Misses

With any accident (big or small), the group safety officer and PI should be contacted immediately (may require a phone call). For serious incidents notify OEHS by calling 801-581-6590. For minor incidents forward incident information via email to the assigned OEHS specialist for Chemistry at questions @oehs.utah.edu.

It will be at the PIs discretion as to how best circulate information of the accident or near miss to the rest of the department. Usually, details of the incident will be shared with all PIs and the Safety Committee (chemsafetycommittee@lists.utah.edu) so that safety issues can be discussed (as appropriate) during group meetings. Alternatively/additionally, the incident may be discussed at the monthly safety officer meetings. This is to ensure that as a whole the department learns from accidents/near misses, and are better prepared.

To help identify and correct unexpected hazards, it is necessary that personnel prepare written reports describing the circumstances of all serious accidents (available on Safety Canvas Site).

One copy of the report should be submitted to the Department OEHS Coordinator (questions@oehs.utah.edu), and one copy should be given to the supervisor of the laboratory in which the accident took place. Reports should be filed within one week of the date of the accident. The submitted copy should bear the original signature of the individual preparing the report.

Written accident reports must be prepared following any of the following incidents:

1. Fires that require extinguishing or the sounding a fire alarm.

2. Any accident that results in an injury requiring medical attention. An injured employee, in conjunction with their supervisor must complete the Worker's First Report of Injury (available from HR) and submit to the HR absence management team as soon as possible following the incident

IX. Working with Chemicals

Researchers must follow the general guidelines given below for working with any chemicals within the department. These are general guidelines, and it is expected that researchers are familiar with the entirety of this Chemical Hygiene Plan (CHP). Chemicals that pose additional risks have more detailed procedures, which are given in the following sections.

A. General Procedure for working with chemicals

1. Be smart and prepared. Follow basic safety rules and be cognizant of the potential hazards. This includes being familiar with the SDS and any additional safety information provided by the chemical supplier (some of this is only available online). Know of the work occurring around you so that you are prepared to help in case of an emergency.

2. *Minimize your exposure*. Wear appropriate PPE, and do not touch "clean" surfaces with gloved hands or contaminate the office with a lab coat. Work in a fume hood or glovebox when applicable/possible.

3. Do not underestimate the risks. Assume the product of your reaction is more toxic/hazardous than the sum of the reagents.

4. Be prepared for accidents. Know what you will do in case the reaction explodes, runs away, catches fire, or spills. This includes knowing where extinguishers and spill kits are and the appropriate methods for cleaning up. Write this information on the hood sash, along with the reaction being run, and notebook page/number.

5. Use and maintain equipment and glassware. Glassware with star cracks can implode/explode under pressure. Glassware with impurities can catalyze side reactions, which may be dangerous/lead to explosions. Equipment that is not properly maintained can lead to frustration or contamination.

6. *Practice good housekeeping*. There is a correlation between orderliness and the level of safety in the lab. The following should always apply:

- Never obstruct access to exits and emergency equipment.
- Store coats, bags, etc. in the appropriate area, not the lab.
- Do not use the floor as a storage area.
- Keep drawers and cabinets closed when not in use.
- Properly label experiments in progress, and glassware that is used to store chemicals.
- Store chemical containers in order and neatly.
- Keep chemical containers closed when not in use.
- Secure gas cylinders (double chained).
- Return chemicals to their storage location when not in use.
- Keep containers at least 2 inches away from edge of benches, to minimize knocking hazards.
- Keep your working area clean and free of clutter. Particularly, keep flammables away, including paper towels.
- Make sure all those connections are properly secure, including those to chilled water.

7. Do not work alone. If you are the only one present in your lab and are setting up/quenching a reaction, find a friend from another lab to come and watch you. Under no circumstances should undergraduate and first year graduate students be working alone.

8. *Work conducted outside of normal hours.* For experiments that will run when no one is around, make sure the hood sash is labeled with the following:

- Name/contact information.
- Details of experiment (usually just the reaction, with ALL products and details on solvent, temperature, etc.)
- Hazards associated with chemicals
- What to do in an emergency
- Notebook page/number of researcher.

Alternatively, if this information is all included in the lab notebook, leaving the notebook open to the specific experiment on the bench top is appropriate.

9. Store Chemicals Appropriately. Ensure that chemicals are properly stored.

10. Transporting chemicals. Make sure to transport all chemicals in an appropriate secondary container.

11. Dispose of waste appropriately. Make sure to dispose of waste in the appropriate stream. Make sure you are familiar with the incompatibilities of the chemicals, and know all products of the reaction before disposing of it (see Appendix F).

B. <u>General Procedure for working with chemicals that have moderate to high</u> <u>chronic toxicity or high acute toxicity</u>

For work with chemicals that have increased toxicity risks, follow the general procedure given below.

1. Follow the procedures outlined above.

2. *Know the toxic risks*. It is the responsibility of the researcher to consult the appropriate literature to know the toxic properties (dose, effects) of the substances being used. If the substance is known to be highly toxic, than no less than two people should be present at all times.

3. Zero skin contact. Consult the chart in Appendix C on glove permeability to choose appropriate gloves, and change them as soon as you know you contaminated them with solvent or the chemical substance, and/or frequently. Wear two gloves if needed. Make sure you are wearing a lab coat and clothes that covers your entire body. If splashing is a concern, use a safety shield. Always wash your hands and arms with soap and water after using these chemicals. In the event of accidental skin contact, flush the affected areas with water and seek medical attention as soon as possible.

4. Use lab hoods. Inhalation of toxic vapors, mists, gases, or dusts can produce poisoning by absorption through the mucous membrane of the mouth, throat, and lungs, and can seriously damage these tissues by local action. Inhaled gases or vapors may pass rapidly into the capillaries of the lungs and be carried into the circulatory system. This absorption can be extremely rapid. Procedures involving volatile toxic substances and those operations involving solid or liquid toxic substances that may result in the generation of aerosols must be conducted in a hood or other suitable containment device. The hood should have been evaluated previously to establish that it is providing adequate ventilation and has an average face velocity of not less than 80 linear ft/min.

5. *Be prepared for accidents*. The laboratory worker should always be prepared for possible accidents or spills involving toxic substances. To minimize hazards from accidental breakage of apparatus or spills of toxic substances in the hood, containers of such substances should generally be stored in pans or trays made of polyethylene or other chemically resistant material and

(particularly in large scale work) apparatus should be mounted above trays of the same type of material. Alternatively, the working surface of the hood can be fitted with a removable liner of adsorbent plastic-backed paper. Such procedures will contain spilled toxic substances in a pan, tray, or adsorbent liner and greatly simplify subsequent cleanup and disposal.

If a major release of a particularly hazardous substance occurs outside the hood, then the room or appropriate area should be evacuated and necessary measures taken to prevent exposure of other workers. OEHS should be contacted (801-581-6590 or 801-585-2677 after hours) for assistance and equipment for spill cleanup; Contaminated clothing and shoes should be thoroughly decontaminated or incinerated.

6. Don't contaminate the environment. Vapors that are discharged from experiments involving particularly hazardous substances should be trapped or condensed to avoid adding substantial quantities of toxic vapor to the hood exhaust air. The general waste disposal procedures outlined above should be followed; however, certain additional precautions should be observed when waste materials are known to contain substances of moderate or high toxicity. Volatile toxic substances should never be disposed of by evaporation in the hood. If practical, waste materials and waste solvents containing toxic substances should be decontaminated chemically by some procedure that can reasonably be expected to convert essentially all of the toxic substances to nontoxic substances (for a discussion, see Prudent Practices for Disposal of Chemicals from Laboratories, pp. 56-100 and Destruction of Hazardous Chemicals in the Laboratory by G. Lunn and E. B. Sansone). If chemical decontamination is not feasible, the waste materials and solvents containing toxic substances should be stored in closed, impervious containers so that personnel handling the containers will not be exposed to their contents. In general, liquid residues should be contained in glass or polyethylene bottles. All containers of toxic wastes should be suitably labeled to indicate the contents (chemicals and approximate amounts) and the type of toxicity hazard that contact may pose. For example, containers of wastes from experiments involving appreciable amounts of weak or moderate carcinogens should carry the warning: CANCER SUSPECT AGENT. All wastes and residues that have not been chemically decontaminated in the exhaust hood where the experiment was carried out should be disposed of in a safe manner that ensures that personnel are not exposed to the material.

7. *Recordkeeping.* Every research group in the department is required to maintain a list of all particularly hazardous substances in use in their laboratories. The Group Safety Officer is responsible for creating and maintaining this list. In addition, records that include amounts of material used and names of workers involved should be kept as part of the laboratory notebook record of all experiments involving particularly hazardous substances.

8. Restrict access to areas where particularly hazardous substances are in use. Those operations involving particularly hazardous substances in which there is the possibility of the accidental release of harmful quantities of the toxic substance must be carried out in designated areas. Specific fume hoods should be designated areas for work with particularly hazardous substances and should be posted with special warning signs indicating that particularly toxic substances may be in use.

Working with extremely toxic substances

All of the procedures and precautions described above should be followed when working with substances known to have high chronic toxicity. In addition, when such substances are to be used in quantities in excess of a few milligrams to a few grams (depending on the hazard posed by the particular substance), the additional precautions described below should also be used.

A substance that has caused cancer in humans or has shown high carcinogenic potency in test animals (but for which a regulatory standard has not been issued by OSHA) will generally require the use of additional precautions. However, this determination will also depend on other factors, such as the physical form and the volatility of the substance, the kind and duration of exposure, and the amount of material to be used. Besides strong carcinogens, substances in the high chronic toxicity category include potent reproductive toxins and certain heavy metal compounds such as dimethylmercury and nickel carbonyl. *Prior to work with these types of substances, researchers should consult with their PI and the safety committee/OEHS to ensure proper training*.

C. General Procedure for working with flammables

Flammable substances are one of the most common hazardous materials found in chemistry labs. These materials readily catch fire and burn in air. Flammable liquids do not burn, rather the vapors of the liquid readily catch fire. How readily a flammable liquid will catch fire is characterized by its flashpoint, which is the minimum temperature at which a liquid gives off enough vapor in sufficient concentration to form an ignitable mixture with air near the surface. Many common lab solvents have flashpoints less than ambient temperature, and thus can pose a major risk, particularly if large spills are not contained.

In addition to following the general guidelines given above, the following should be considered when handling flammable solvents:

1. *Handle flammables in areas free of ignition sources*. This includes open flames, electrical equipment (esp. motors), static electricity, and for certain chemicals, heat.

2. Never heat a flammable substance with an open flame.

3. When transferring flammable liquids in metal equipment, static-generated sparks should be avoided by grounding the system. This is particularly true for solvent kegs and other large-volumes of flammables.

4. Use a hood for proper ventilation. Make sure that the hood is free of clutter. Flammable liquids should always be covered, and the hood free of material that can readily spread a fire, such as paper towels.

5. Safety goggles, gloves, and a cotton or nomex labcoat should be worn.

6. Be prepared for spills. In case of a major spill on the floor, immediately turn the main power supply of the lab off, solicit help, and clean up with spill pads. In case of a major spill in the hood, immediately unplug all electrical equipment and clean up with spill pads.

7. *Know what extinguisher to use in case of a fire*. Any that is labeled with a "B" will work for putting out flammable substances. Note - if pyrophoric metals are also present, then a "D" extinguisher or sand is required.

D. General Procedure for working with explosive hazards

In addition to following the general guidelines given above, the following should be considered when handling explosives, or potential explosive hazards.

- 1. *Know the risks, consult, and plan well*. It is the responsibility of the researcher to evaluate the explosive hazards involved in all experiments they are performing and how to minimize the risk of explosions. This may include working in the dark. Researchers should also work with small quantities, and only scale-up after having consulted with the PI and safety committee. *Use of explosive chemicals for the first time will require the researcher to fill out a departmental assessment form.*
- 2. If possible, use a safer alternative.
- 3. Use appropriate PPE and engineering controls. The use of Kevlar sleeves/gloves, a face shield, and a blast shield is recommended. Work should be done in a clean hood or glovebox.
- 4. Assume an explosion will happen. Have spill kits, fire extinguishers, etc. handy and know how you will clean up the explosion.
- 5. *Tell others in the group what you are doing*. Be sure that they are ready to help if the worst happens.

<u>Organic Peroxides</u>

- Limit the quantity or peroxide to the minimum amount required. Do not return unused peroxide to the container.
- Clean up all spills immediately. Peroxide solutions can be absorbed on vermiculite or other absorbing material and disposed of harmlessly according to OEHS procedures.
- Reduce the sensitivity of most peroxides to shock and heat by dilution with inert solvents, such as aliphatic hydrocarbons. However, do not use aromatics, which are known to induce the decomposition of diacyl peroxides.
- Do not use solutions of peroxides in volatile solvents under conditions in which the solvent might vaporize because this will increase the peroxide concentration in the solution.
- Do not use metal spatulas to handle peroxides because contamination by metals can lead to explosive decomposition. Magnetic stirring bars can unintentionally introduce iron, which can initiate an explosive reaction of peroxides. Ceramic, Teflon, or wooden

spatulas and stirring blades may be used if it is known that the material is not shock sensitive.

- Do not permit open flames and other sources of heat near peroxides. It is important to label areas that contain peroxides so that this hazard is evident.
- Avoid friction, grinding, and all forms of impact near peroxides, especially solid peroxides. Glass containers that have screw-cap lids or glass stoppers should not be used. Polyethylene bottles that have screw-cap lids may be used.
- To minimize the rate of decomposition, store peroxides at the lowest possible temperature consistent with their solubility or freezing point. Do not store liquid peroxides or solutions at or lower than the temperature at which the peroxide freezes or precipitates because peroxides in these forms are extremely sensitive to shock and heat.

Peroxidizable Compounds

• *Test peroxide forming chemicals*. Class B chemicals should be tested every 3 months for peroxides. This is readily done with peroxide test strips that can be purchased from Sigma Aldrich (0-100 ppm test range). **Peroxide levels should be noted on the bottle**. Low concentrations of peroxides can generally be removed by filtering the contaminated material through a column of chromatography-grade basic alumina (refer to PP for more details). If testing on any chemical shows more than 100 ppm peroxides, or researchers notice that the chemical has an unusual consistency (e.g., the diethyl ether has a gooey consistency), they should notify OEHS immediately for disposal.

If a container of Class A peroxidizables is past its expiration date or if the presence of peroxides is suspected/determined, do not attempt to open the container. *Call OEHS immediately* and warn others of the potential (deadly) danger.

E. <u>Materials that Require Special Attention Because of Toxicity, Reactivity,</u> <u>Explosivity, or Chemical Incompatibility.</u>

Below we list several chemicals that require additional precautions. Those that are considered particularly hazardous substances are indicated with PHS.

• Acetylenic compounds, both organic and inorganic (especially heavy metal salts), can be explosive and shock sensitive. At pressures of 2 atm or greater and moderate temperature, acetylene (C₂H₂) has been reported to decompose explosively, even in the absence of air. Because of these dangers, *acetylene must be handled in acetone solution and never stored alone in a cylinder*.

- Acrylonitrile (PHS) is regulated as a probable human carcinogen by OSHA and also is listed as a substance with a moderate degree of acute toxicity (oral LD₅₀ (rat) is 78 mg/kg). The PEL (permissible exposure limit) is 2 ppm; the TLV-TWA (threshold limit value time-weighted average) is also 2 ppm. Acrylonitrile is severely irritating to the eyes and mildly irritating to the skin; prolonged contact with the skin can lead to burns. Acrylonitrile is a highly flammable liquid; its vapor forms explosive mixtures with air. Work with acrylonitrile should be conducted in a fume hood to prevent exposure by inhalation; splash goggles and impermeable gloves should be worn at all times to prevent eye and skin contact.
- Alkyllithium compounds are highly reactive and pyrophoric. Violent reactions may occur on exposure to water, carbon dioxide, and other materials. Alkyllithium compounds are highly corrosive to the skin and eyes. *tert*-Butyllithium solutions are the most pyrophoric and may ignite spontaneously on exposure to air. Contact with water or moist materials can lead to fires and explosions. These compounds should be stored and handled under an inert atmosphere in areas that are free from ignition sources.
- Aluminum chloride (AlCl₃) should be considered a potentially dangerous material. If moisture is present, sufficient decomposition may form hydrogen chloride (HCl) and build up considerable pressure. If a bottle is to be opened after long storage, it should first be completely enclosed in a heavy towel.
- Ammonia and amines. Ammonia (NH₃) reacts with iodine to give nitrogen triiodide, which explodes on touch. Ammonia reacts with hypochlorites (bleach) to give chlorine. Mixtures of ammonia and organic halides sometimes react violently when heated under pressure. Ammonia is combustible. Inhalation of concentrated fumes can be fatal. Ammonia and amines can react with heavy metal salts to produce explosive fulminates.
- Azides, both organic and inorganic, and some azo compounds can be heat and shock sensitive. Azides such as sodium azide can displace halide from chlorinated hydrocarbons such as dichloromethane to form highly explosive organic polyazides; this substitution reaction is facilitated in solvents such as dimethyl sulfoxide.
- **Benzene** (PHS). Exposure to benzene can lead to both chronic as well as acute toxic effects. The acute toxic effects from skin contact, inhalation, or ingestion of benzene are low. In humans, acute inhalation exposure to benzene can produce a picture of acute delirium, characterized by excitement, euphoria, and restlessness and, if the exposure is significantly high, the symptoms may progress to depression, drowsiness, stupor, and even unconsciousness. The concentration required to produce this symptom complex is 1000 ppm or higher. These concentrations will also produce irritation of the eye, nose, and respiratory tract.

Chronic inhalation exposure to 25-50 ppm of benzene can produce changes in the blood picture that include macrocytosis, decrease in the total red blood count, decrease in platelets, decrease in the hemoglobin concentration, or decrease in leukocytes. Any or all of these hematologic effects may be seen in any individual. Usually, the worker will be

asymptomatic while these effects are observed in the blood picture. Continued exposure at somewhat higher concentrations (probably more than 100 ppm) can insidiously result in more severe blood disorders that include leukopenia or even aplastic anemia, with symptoms of headaches, dizziness, loss of appetite, nervousness, irritability, and perhaps bleeding manifestations, i.e., nosebleeds, easy bruisability, or hematuria. Severe cases may have fatal outcomes. Recently, a number of reports have been published that describe leukemia in workers who have had aplastic anemia. These cases have been reported in Italy and Turkey in workers exposed to grossly high concentrations of benzene. In addition, there is some indication that an excess of leukemia may occur without a preceding picture of aplastic anemia in workers who have been repeatedly exposed to benzene at concentrations of more than 100 ppm.

The current OSHA PEL (permissible exposure limit) for benzene is 1 ppm as an 8-hour timeweighted average (TWA), 25 ppm for a ceiling concentration for time period such that the 8-hour TWA is not exceeded, and a peak above the ceiling of 50 ppm for no more than 10 min. The ACGIH TLV-TWA value is 10 ppm. Benzene is a flammable liquid and should not be exposed to heat or flame. An explosion hazard also exists when its vapors are exposed to flame. Benzene may react vigorously with oxidizing agents such as bromine pentafluoride, chlorine, chromic acid, nitryl perchlorate, oxygen, ozone, perchlorates, aluminum chloride plus fluorine perchlorate, sulfuric acid plus permanganates, potassium peroxide, silver perchlorate plus acetic acid, and sodium peroxide.

• **Bis(chloromethyl)ether (BCME), Chloromethyl Methyl Ether, and Other Chloromethyl Ether Derivatives** (PHS). Because of the high volatility of bis(chloromethyl)ether (BCME), inhalation is the route of exposure that presents the greatest hazard to humans. BCME vapor is severely irritating to the skin and mucous membranes and can cause corneal damage that heals slowly. The substance has caused lung cancer in humans. BCME is highly toxic to animals via inhalation: LD50 (rats, 7-hour inhalation) = 7 ppm. It is moderately toxic via the oral and skin routes: LD50 (rats, oral) = 280 mg/kg; LD50 (rabbits, skin) = 368 mg/kg. Its vapors are strongly irritant to the eyes of rats. Rats and hamsters subjected to 10 or 30 6-hour exposures of 1 ppm BCME showed evidence of tracheal and bronchial hyperplasia, as well as effects on the central nervous system. BCME is carcinogenic to mice following inhalation, skin application, or subcutaneous administration. BCME is a lung carcinogen in humans.

The TLV (threshold limit value) for BCME is 0.001 ppm (1 ppb; 5 mg/m3). The substance is classified by ACGIH as a human carcinogen. OSHA has classified BCME as a cancer-suspect agent and has stringent regulations (29 CFR 1910.1008) for its use if its concentration in a material exceeds 0.1%.

- Boron halides are powerful Lewis acids and hydrolyze to strong protonic acids.
- **Carbon disulfide** (CS₂) is both very toxic and very flammable; mixed with air, its vapors can be ignited by a steam bath or pipe, a hot plate, or a light bulb.

• **Carbon Monoxide** (PHS). Carbon monoxide is a direct and cumulative poison. It combines with the hEMPglobin of the blood to form a relatively stable compound (carboxyhemoglobin) rendering it useless as an oxygen carrier. When about one-third of the hemoglobin has entered into such combination, the victim dies. Since carbon monoxide is odorless, colorless, and tasteless, it has no warning properties. Exposure to 1500-2000 ppm CO in air for 1 hour is dangerous, and exposure to 4000 ppm is fatal in less than 1 hour. Headache and dizziness are the usual symptoms of CO poisoning, but occasionally the first evidence of poisoning is the collapse of the patient. Pregnant women are more susceptible to the effects of carbon monoxide exposure.

Carbon monoxide should be used only in areas with adequate ventilation. A trap or vacuum break should always be used to prevent impurities from being sucked back into a CO cylinder. *Cylinders with regulators attached MUST have a working detector on it (these can be purchased from Home Depot or other hardware stores)*.

• **Carbon Tetrachloride** (PHS). The current OSHA PEL (permissible exposure limit) and ACGIH TLV (threshold limit value) for carbon tetrachloride are 2 ppm as an 8-hour time-weighted average and 5 ppm as a ceiling for any period of time provided the 8-hour average is not exceeded. ACGIH states that skin contact may account for a substantial part of toxic responses.

The acute toxicity of carbon tetrachloride by all routes of exposure is low to moderate (oral LD50 in rats is 2,350 mg/kg). Carbon tetrachloride shows carcinogenic effects in animal studies and is listed in group 2B ("possible human carcinogen") by IARC. In most of its uses in Chemistry Department laboratories it need not be treated as a particularly hazardous substance. All operations should be carried out in a hood, not only because of the carcinogenicity of the substance, but also because of its other toxic effects (e.g., hepatotoxicity) and its volatility. Nitrile rubber is the recommended material for gloves and other protective clothing.

• Chlorine (PHS). C1₂ is highly toxic and may react violently with hydrogen (H₂) or with hydrocarbons when exposed to sunlight.

Chlorine is a severe irritant of the eyes, skin, and mucous membranes. Inhalation may cause coughing, choking, nausea, vomiting, headache, dizziness, difficulty breathing, and delayed pulmonary edema, which can be fatal. Exposure to ca. 500 pm for 30 minutes may be fatal and 1000 ppm can be lethal after a few breaths. Chlorine is highly irritating to the eyes and skin; exposure to 3-8 ppm causes stinging and burning of the eyes, and contact with liquid chlorine or high concentrations of the vapor can cause severe burns. Chlorine can be detected by its odor below the permissible limit; however, because of olfactory fatigue, odor may not always provide adequate warning of the presence of harmful concentrations of this substance. There is no evidence for carcinogenicity or reproductive or developmental toxicity of chlorine in humans. The LC50 for inhalation (rat) is 293 ppm (1 h); the PEL (permissible exposure limit) is 1 ppm while the TLV-TWA (threshold limit value – time-weighted average) is 0.5 ppm.

Chlorine is noncombustible but is a strong oxidizer and will support combustion of most flammable substances, sometimes with explosive violence. Cylinders of chlorine should be stored in locations appropriate for compressed gas storage and separated from incompatible compounds such as hydrogen, acetylene, ammonia, and flammable materials. Because of its high toxicity, laboratory operations using chlorine must be carried out in a hood.

• Chloroform (PHS). The acute toxicity of chloroform is classified as moderate by ingestion and low by inhalation. Inhalation exposure to chloroform at concentrations greater than 1000 ppm can produce dizziness, nausea, and headaches. At higher concentrations, there can be disorientation and delirium progressing to unconsciousness. Such high exposure can also produce liver and possibly kidney damage. It is believed that chloroform can sensitize the heart to adrenaline, so it may cause cardiac arrhythmias and possibly death. High concentrations of the vapor can produce conjunctivitis. Liquid chloroform in the eyes will produce a painful corneal injury that usually heals in several days.

Chronic exposure to chloroform at concentrations of 100-200 ppm has been reported to produce large livers. Continued contact with the skin can produce drying, fissuring, and inflammation. In experimental studies, prolonged ingestion of high levels of chloroform by mice resulted in liver cancers and by rats, kidney tumors. Chloroform has produced embryo toxicity in experimental animals. It is a suspected human carcinogen.

Although the fire hazard of chloroform is slight, exposure to heat or flame can result in generation of phosgene gas. Chloroform reacts violently with acetone in the presence of base, and with aluminum, disilane, lithium, magnesium, nitrogen tetroxide, potassium, perchloric acid plus phosphorus pentoxide, potassium hydroxide plus methanol, potassium tert-butoxide, sodium, sodium hydroxide plus methanol, sodium methylate, and sodium hydride.

The current OSHA PEL (permissible exposure limit) for chloroform is 50 ppm as an 8-hour timeweighted average. This standard is also a ceiling level that should not be exceeded for any 15-min period. The ACGIH currently recommends that chloroform be treated as a suspect human carcinogen and recommends an 8-hour time weighted average exposure of 10 ppm.

Although chloroform has caused tumors in animals, its potency is low. In most of its uses in the Chemistry Department it need not be treated as a particularly hazardous substance. In cases where significant quantities of chloroform are in frequent use, the general procedures outlined in Part VI-C should provide adequate protection. The high volatility of chloroform emphasizes the importance of a hood for such operations. Polyvinyl alcohol gloves provide the best hand protection.

• **Diazomethane** (CH₂N₂) and related diazo compounds should be treated with extreme caution. They are very toxic, and the pure gases and liquids explode readily even from contact with sharp edges of glass. Solutions in ether are safer from this standpoint. An ether solution of diazomethane is rendered harmless by dropwise addition of acetic acid.

- **Diethyl and other ethers**, including tetrahydrofuran and 1,4-dioxane and particularly the branched-chain type of ethers, may contain peroxides that have developed from air autoxidation. Concentration of these peroxides during distillation may lead to explosion. Ferrous salts or sodium bisulfite can be used to decompose these peroxides, and passage over basic active alumina can remove most of the peroxidic material. In general, however, dispose of old samples of ethers if they test positive test for peroxide.
- **Diisopropyl ether** is a notoriously dangerous, Class A peroxide former. The peroxide is not completely soluble in the mother liquor. Peroxide concentrations from autoxidation may form saturated solutions that then crystallize the peroxide as it is being formed. There are numerous reports of old bottles of diisopropyl ether being found with large masses of crystals settled at the bottom of the bottle. These crystals are extremely shock sensitive, even while wetted with the diisopropyl ether supernatant. Mild shock (e.g., bottle breakage, removing the bottle cap) is sufficient to result in explosion. This ether should not be stored in the laboratory. Only the amount required for a particular experiment or process should be purchased; any leftover material should be disposed of immediately.
- Dimethyl and Diethyl Sulfate (PHS). Many cases of dimethyl sulfate poisoning have been reported. The common initial symptoms are headache and giddiness, with burning of the eyes. The patient's condition may worsen, with painful eyes, nose and throat irritation, loss of voice, coughing, difficulty in breathing and swallowing, vomiting, and diarrhea possible. The onset of the symptoms may be delayed up to 10 hours. This substance is extremely hazardous because of its lack of warning properties and its delayed toxic effects. Skin contact causes blistering and necrosis, and DMS can be absorbed through the skin in sufficient quantity to cause systemic intoxication. In the worst cases, there is severe inflammation of the mucous membranes and pulmonary injury that may be fatal; several deaths have occured. For example, exposure to 97 ppm for 10 min was fatal. DMS is moderately toxic to animals via the oral route: LD50 (rats) = 440 mg/kg. Undiluted DMS produced moderate to severe irritation when applied to the skin of guinea pigs; 1% DMS produced mild irritation.

DMS does not cause skin sensitization in animals. Undiluted DMS applied to rabbit eyes produced severe injury. Even a 1-hour exposure to 58 ppm has resulted in permanent eye damage in rats. During a 4-hour exposure, 30 ppm DMS killed five out of six rats, but 15 ppm was not lethal. DMS has been shown to be carcinogenic in the rat by inhalation, subcutaneous injection, and following 1 hour per day exposures to 10 ppm DMS for 130 days. The TLV (threshold limit value) for DMS is 0.1 ppm (0.5 mg/m3) as an 8-hour time-weighted average. DMS is classified as being suspected of carcinogenic potential in humans by the ACGIH. The OSHA PEL (permissible exposure limit) for DMS is 1.0 ppm. These limits include a warning of the potential contribution of skin absorption to the overall exposure.

It is particularly important to avoid skin contact by the appropriate use of rubber gloves, a rubber apron, and other protective apparel, and to avoid inhalation of even low concentrations of vapor by working in a hood.

- **Dimethyl sulfoxide** (DMSO), (CH₃)₂SO, decomposes violently on contact with a wide variety of active halogen compounds, such as acyl chlorides. Explosions from contact with active metal hydrides have been reported. DMSO does penetrate and carry dissolved substances through the skin membrane.
- Dry benzoyl peroxide (C₆H₅CO₂)₂ is easily ignited and sensitive to shock. It decomposes spontaneously at temperatures greater than 50 °C. It is reported to be desensitized by addition of 20% water.
- Dry ice should not be kept in a container that is not designed to withstand pressure. Containers of other substances stored over dry ice for extended periods generally absorb carbon dioxide (CO₂) unless they have been carefully sealed. When such containers are removed from storage and allowed to come rapidly to room temperature, the CO₂ may develop sufficient pressure to burst the container with explosive violence. On removal of such containers from storage, the stopper should be loosened or the container itself should be wrapped in towels and kept behind a shield. Dry ice can produce serious burns, as is also true for all types of dry-ice cooling baths.
- **Dusts** that are suspensions of oxidizable particles (e.g., magnesium powder, zinc dust, carbon powder, and flowers of sulfur) in the air can constitute powerful explosive mixtures. These materials should be used with adequate ventilation and should not be exposed to ignition sources. When finely divided, some solids, including zirconium, titanium, Raney nickel, lead (such as prepared by pyrolysis of lead tartrate), and catalysts (such as activated carbon containing active metals and hydrogen), can combust spontaneously if allowed to dry while exposed to air and should be handled wet.
- Ethylene Dibromide (1,2-Dibromoethane) (PHS). Ethylene dibromide (EDB) is classified as a compound with a moderate degree of acute toxicity; the approximate oral lethal dose of EDB for humans is 5-10 mL. Skin absorption of EDB can also cause death, and inhalation of the vapor can produce pulmonary edema. EDB can cause severe irritation to all exposed tissues, respiratory tract, skin, and eye. Systemic effects include central nervous system depression, kidney injury, and severe liver necrosis. Ethylene dibromide is highly toxic to animals via inhalation. The maximum survival exposure of rats to EDB vapors in air are 3000 ppm for 6 min, 400 ppm for 30 min, and 200 ppm for 2 hours. It is moderately toxic via the oral and skin routes: LD50 (rats, oral) = 108 mg/kg; LD50 (rabbits, skin) = 300 mg/kg. EDB is markedly irritating to skin, and a 10% solution has caused serious but reversible corneal injury in rabbit eyes. Rats were repeatedly exposed to 50 ppm EDB for 6 months. Half died from pneumonia and upper respiratory tract infections. Slight changes in the liver and kidney were seen. EDB has induced a high incidence of tumors (squamous-cell carcinomas of the forestomach) in mice and rats following oral administration. The 1979 TLV (threshold limit value) for EDB was 20 ppm (155 mg/m3) as an 8-hour time-weighted average. The exposure limit is 30 ppm over any 15-min period. These limits include a warning about the potential contribution of skin absorption to the overall exposure. In 1980, the ACGIH put EDB in category A 1b (human carcinogen). For this category, there is no assigned TLV (threshold limit value), but the ACGIH recommends that those working with A1b carcinogens should be properly equipped to

ensure virtually no contact with the carcinogens. The OSHA PEL (permissible exposure limit) for EDB is 20 ppm, and the acceptable maximum peak is 50 ppm for 5 min in any 8-hour time period.

Serious skin injury can occur from direct exposure to EDB. The substance can penetrate neoprene and several other types of plastic; therefore, gloves and other protective apparel made of these materials provide only temporary protection if EDB spills on them.

- Ethylene oxide (C₂H₄O) has been known to explode when heated in a closed vessel. Experiments using ethylene oxide under pressure should be carried out behind suitable barricades.
- **Fluorine** (F₂) is an extremely toxic reactive oxidizing gas with extremely low permissible exposure levels. Only trained personnel should be authorized to work with fluorine. *Anyone planning to work with fluorine must fill out a departmental SOP and consult with the safety committee*.
- Halogenated compounds, such as chloroform (CHCl₃), carbon tetrachloride (CCl₄), and other halogenated solvents, should not be dried with sodium, potassium, or other active metals; violent explosions usually result. Many halogenated compounds are toxic. Oxidized halogen compounds—chlorates, chlorites, bromates, and iodates—and the corresponding peroxy compounds may be explosive at high temperatures.
- Hydrazine (PHS). Hydrazine is classified as a compound with a high degree of acute toxicity; exposure to its vapors can cause respiratory tract irritation, excitement, convulsion, cyanosis, and decrease in blood pressure. The liquid can severely burn the eyes and skin. Hydrazine can cause fatty degeneration of the liver, nephritis, and hemolysis. Hydrazine also poses a dangerous fire and explosion risk and can explode during distillation if traces of air are present. Hydrazine is moderately toxic to animals via the inhalation, oral, and skin routes: LC50 (rats, 4-hour inhalation) = 570 ppm; LD50 (rats, oral) = 60 mg/kg; LD50 (rabbits, skin) = 283 mg/kg (hydrazine hydrate). It is a strong skin and mucous membrane irritant and a strong skin sensitizer. Hydrazine hydrate produced moderately severe irritation when applied to rabbit eyes. After repeated oral, skin, or injection exposure, the effects noted include weight loss, weakness, vomiting, and convulsions. The chief histological finding is fatty degeneration of the liver. Among guinea pigs and dogs exposed to hydrazine in the air 5-47 times, the dogs showed liver damage, with lesser damage to the kidneys and lungs, while the guinea pigs had pneumonitis and partial lung collapse. Hydrazine is not regarded as having adequate warning properties.

Hydrazine and hydrazine salts have been shown to be carcinogenic in mice after oral and intraperitoneal administration and in rats following oral dosing. By the oral route, effects were found at doses of 24-36 (mg/kg)/day in mice and 20 (mg/kg)/day in rats. No tumors were observed in Syrian golden hamsters after oral administration. The ACGIH has classified hydrazine as suspected of carcinogenic potential in humans. The TLV (threshold limit value) for hydrazine is 0.1 ppm (0.1 mg/m3) and the OSHA PEL (permissible exposure limit) is 1.0 ppm (1 mg/m3) as 8-hour timeweighted averages. These limits

include a warning about the potential contribution of skin absorption to the overall exposure. NIOSH has (1978) recommended a ceiling limit of 0.03 ppm in any 2-hour period.

Nitrile rubber is recommended for gloves and other protective apparel. Prompt washing with water effectively removes hydrazine from skin that it has splashed on. Hydrazine should not be used in the vicinity of a flame or under conditions where sparks can occur, as an explosion or fire can result.

• **Hydrogen fluoride and hydrogen fluoride generators (PHS).** Anyone planning to work with fluorine must fill out a departmental SOP and consult with the safety committee.

All forms — dilute or concentrated solutions or the vapor — of hydrofluoric acid (HF) cause severe burns. Inhalation of anhydrous HF or HF mist or vapors can cause severe respiratory tract irritation that may be fatal. Death from pulmonary edema occurred within 2 hours in three of six workers splashed with 70% HF solution despite prompt showering with water. Anhydrous HF is a clear, colorless liquid that boils at 19.5°C. Because of its low boiling point and high vapor pressure, anhydrous HF must be stored in pressure containers. A 70% aqueous solution is a common form of HF. Hydrofluoric acid is miscible with water in all proportions and forms an azeotrope (38.3% HF) that boils at 112°C. Anhydrous or concentrated aqueous HF causes immediate and serious burns to any part of the body. Dilute solutions ($\leq 30\%$) and gaseous HF are also harmful, although several hours may pass before redness or a burning sensation is noticed. These burns may still be quite severe and progressively damaging to the skin and deeper tissues. "Undissociated HF readily penetrates skin and deep tissue where the corrosive fluoride ion can cause necrosis of soft tissues and decalcification of bone; the destruction produced is excruciatingly painful. Fluoride ion also attacks enzymes (e.g. of glycolysis) and cell membranes. The process of tissue destruction and neutralization of the hydrofluoric acid is prolonged for days, unlike other acids that are rapidly neutralized. Because of the insidious manner of penetration, a relatively mild or minor exposure can cause a serious burn" [Proctor, N. H.; Hughes, J. P.; Fischman, M. L. Chemical Hazards of the Workplace, J. B. Lippincott Co., Philadelphia, 1988, p. 279]. Occasionally workers fail to recognize the importance of seeking medical attention for HF burns before pain commences. By the time the victim is affected with progressively deep and more painful throbbing and burning, serious damage may have taken place. Exposures under fingernails can be a particularly painful problem if ignored. Wearing clothing (including leather shoes and gloves) that has absorbed small amounts of HF can result in serious delayed effects such as painful slow-healing skin ulcers.

When handling HF, it is crucial to ensure adequate ventilation by working only in a hood so that safe levels (3 ppm) are not exceeded. All contact of the vapor of the liquid with eyes, skin, respiratory system, or digestive system must be avoided by using protective equipment such as a face shield and neoprene or polyvinyl chloride gloves. The protective equipment should be washed after each use to remove any HF on it. Safety showers and eyewash fountains should be nearby. Anyone working with HF should have received prior

instructions about its hazards and in proper protective measures and should know the recommended procedure for treatment in the event of exposure (Reinhardt, C.F. et al.; Am. Ind. Hyg. Assn. J., 1966, 27, 166).

- *Spills and leaks* The vapors of both anhydrous HF and aqueous 70% HF produce visible fumes if they contact moist air. This characteristic can be useful in detecting leaks but cannot be relied on because of atmospheric variations. Spills of HF must be treated immediately to minimize the dangers of vapor inhalation, body contact, corrosion of equipment, and possible generation of hazardous gases. Spills should be contained and diluted with water. The resulting solution should be neutralized with lime before disposal.
- *Waste disposal* Waste HF should be slowly added to a larger volume of a stirred solution of slaked lime to precipitate calcium fluoride, which is chemically inert and poses little toxic hazard (sodium fluoride is highly soluble and toxic). Alternatively, hydrofluoric acid can be diluted to about 2% concentration with cold water in a polyethylene vessel, neutralized with aqueous sodium hydroxide, and treated with excess calcium chloride solution to precipitate calcium fluoride.
- *In the event of exposure* Anyone who knows or even suspects that he or she has come into direct contact with HF should immediately flush the exposed area with large quantities of cool water. Exposed clothing should be removed as quickly as possible while flushing. Medical attention should be obtained promptly, even if the injury appears slight. On the way to the physician, the burned area should be immersed in a mixture of ice and water. If immersion is impractical, a compress made by inserting ice cubes between layers of gauze should be used. Make sure that the physician understands that the injury was caused by HF and requires treatment very different from other acid burns. Even in the case of very small exposure, washing alone may not be sufficient to completely prevent injury. For minor exposures such as small hole in a glove, application of a calcium glutaconate antidote gel can bind free fluoride ion not removed by washing. For regular HF users, this gel may be obtained by contacting the OEHS Office (801-581-6590).
- If HF liquid or vapor has contacted the eyes, these organs should be flushed with large quantities of clean water while the eyelids are held apart This flushing should be continued for 15 minutes.

Medical attention should be obtained promptly.

- Anyone who has inhaled HF vapor should be removed immediately to an uncontaminated atmosphere and kept warm. Medical help should be obtained promptly. Anyone who has ingested HF should drink a large quantity of water as quickly as possible. Do not induce vomiting. Again, medical help should be obtained promptly. After the acid has been thoroughly diluted with water, if medical attention is delayed, the person should be given milk or two fluid ounces of milk of magnesia to drink to sooth the burning effect.
- **Hydrogen peroxide** (H₂O₂) stronger than 3% can be dangerous; in contact with skin, it causes severe burns. Thirty percent H₂O₂ may decompose violently if contaminated with iron, copper, chromium, or other metals or their salts. Stirring bars may inadvertently bring metal into a reaction and should be used with caution.

- **Hydrogen Sulfide** (PHS). The acute toxicity of hydrogen sulfide by inhalation is moderate. A five minute exposure to 800 ppm has resulted in death. Inhalation of 1000 to 2000 ppm may cause coma after a single breath. Exposure to lower concentraions may cause headache, dizziness, and nausea. Low concentrations (20-150 ppm) of hydrogen sulfide can cause eye irritation which may be delayed in onset. Although the odor of hydrogen sulfide is detectable at very low concentrations (below 0.1 ppm), it rapidly causes olfactory fatigue at higher levels, and therefore is not considered to have adequate warning properties. Hydrogen sulfide has not been shown to be carcinogenic or to have reproductive or developmental effects in humans. The hydrogen sulfide LC50 for inhalation (rat) is 444 ppm; the PEL (permissible exposure limit) ceiling is 20 ppm, and the TLV-TWA (threshold limit value - timeweighted average) is 10 ppm. Hydrogen sulfide is flammable in air, and the combustion products are also toxic by inhalation. It is incompatible with strong oxidizers, will attack many metals, some plastics and rubbers, and reacts violently with a variety of metal oxides. Laboratory operations with hydrogen sulfide should be carried out in a hood. In particular, cylinders of hydrogen sulfide should be stored and used in a continuously ventilated gas cabinet or fume hood.
- Mercury. The element mercury is a liquid metal with a vapor pressure of 0.00185 mm at 25°C. This corresponds to a saturation concentration of 20 milligrams of mercury per cubic meter of air or 2.4 parts per million of air. The American Conference of Governmental Industrial Hygienists has established a threshold limit for mercury vapor of 0.05 milligrams of mercury per cubic meter of air for continuous 40-hour per week exposure. Long term chronic exposure to mercury vapor in excess of 0.05 mg of mercury per cubic meter of air may result in cumulative poisoning. The use of mercury in laboratory amounts in well-ventilated areas is fairly safe; however special precautions must be followed when working with large quantities of mercury.

Mercury poisoning from exposure by chronic inhalation produces a variety of symptoms. The characteristic effects are emotional disturbances, unsteadiness, inflammation of the mouth and gums, general fatigue, memory loss, and headaches. Kidney damage may result from poisoning by mercurical salts. In most cases of exposure by chronic inhalation, the symptoms of poisoning gradually disappear when the source of exposure is removed. However, improvement may be slow and complete recovery may take years. Skin contact with mercury compounds produces irritation and various degrees of corrosion. Soluble mercury salts can be absorbed through the intact skin and produce poisoning.

Every effort should be made to prevent spills of metallic mercury because the substance is extremely difficult and time consuming to pick up. Droplets get into cracks and crevices, under table legs, and under and into equipment. If spills are frequent and Hg is added to the general air level, the combined concentration may exceed the allowable limits.

Storage — Containers of large quantities of mercury should be kept closed and stored in secondary containers in a well-ventilated area. When breakage of instruments or apparatus containing mercury is a possibility, the equipment should be placed in an enameled or plastic tray or pan that can be cleaned easily and is large enough to contain the mercury in

the event of accident. Transfers of Hg from one container to another should be carried out in a hood, over a tray or pan to confine any spills.

Clean Up of spills— Pools of metallic Hg can be collected by suction by using an aspirator bulb or a vacuum device made from a filtering flask, a rubber stopper, and several pieces of flexible rubber and glass tubing. Alternatively, mercury-spill cleanup kits are available from OEHS. When a large spill, pressure system rupture, or heating of mercury is involved, the OEHS Office (801-581-6590) will be glad to survey the area and advise on the degree of hazard which may exist and necessary preventive measures to be undertaken. If Hg has spilled on the floor, the workers involved in cleanup and decontamination activities should wear plastic shoe covers. When the cleanup is complete, the shoe covers should be disposed of and the workers should thoroughly wash their hands, arms, and face several times.

Waste Disposal — Significant quantities of metallic Hg from spills or broken thermometers or other equipment, and contaminated Hg from laboratory activities should be collected in thick- walled high-density polyethylene bottles for reclamation. Rags, sponges, shoe covers, and such used in cleanup activities, and broken thermometers containing small amounts of residual mercury, should be placed in a sealed plastic bag, labeled, and disposed of as hazardous waste.

- Nickel Carbonyl (PHS). The use of nickel carbonyl should be avoided if at all possible. *The use of nickel carbonyl requires prior approval from the Chemistry Department Safety Committee.*
- Nitric acid is a strong acid, very corrosive, and decomposes to produce nitrogen oxides. The fumes are very irritating, and inhalation may cause pulmonary edema. Nitric acid is also a powerful oxidant and reacts violently, sometimes explosively reducing agents (e.g., organic compounds) with liberation of toxic nitrogen oxides. Contact with organic matter must be avoided. Extreme caution must be taken when cleaning glassware contaminated with organic solvents or material with nitric acid. Toxic fumes of NOx are generated and explosion may occur.
- N-Nitrosodialkylamines and Certain Other N-Nitroso Compounds (PHS). N-Nitrosodimethylamine is strongly hepatotoxic and can cause death from liver insufficiency in experimental animals. It is carcinogenic in at least 10 animal species, and is regarded to be a probable human carcinogen. The main targets for its carcinogenic activity are the liver, lung, esophagus, trachea, and nasal cavity. Although data are not available on the toxicity N-nitrosodiethylamine in humans. the closely related compound of Nnitrosodimethylamine has caused extensive liver damage as a consequence of ingestion, inhalation, or topical application to the skin. It is prudent to regard other nitrosamine derivatives as being potential carcinogens.

All work with N-nitrosodialkylamines should be carried out in a well-ventilated hood or in a glove box equipped with a HEPA filter. To the extent possible, all vessels that contain N-nitrosodialkylamines should be kept closed. All work should be carried out in apparatus that is contained in or mounted above unbreakable pans that will contain any spill. All containers should bear a label such as the following: CANCER-SUSPECT AGENT. All personnel who handle the material should wear plastic, latex, or neoprene gloves and a fully buttoned laboratory coat.

Storage — All bottles of N-nitrosodialkylamines should be stored and transported within an unbreakable outer container; storage should be in a ventilated storage cabinet (or in a hood).

Clean Up of spills and waste disposal — Because N-nitrosodialkylamines are chemically stable under usual conditions, disposal is best carried out by incineration. Contact the Environmental Management Office to arrange for the disposal of waste and contaminated materials. For incineration of liquid wastes, solutions should be neutralized if necessary, filtered to remove solids, and put in closed polyethylene containers for transport. All equipment should be thoroughly rinsed with solvent, which should then be added to the liquid waste for incineration. Great care should be exercised to prevent contamination of the outside of the solvent container. If possible, solid wastes should be incinerated; if this is not possible, solid wastes from reaction mixtures that may contain Nnitrosodialkylamines should be extracted and the extracts added to the liquid waste. Similarly, any rags, paper and such that may be contaminated should be incinerated. Contaminated solid materials should be enclosed in sealed plastic bags that are labeled CANCER-SUSPECT AGENT and with the name and amount of the carcinogen. The bags should be stored in a well-ventilated area until they are incinerated. Spills of Nnitrosodialkylamines can be absorbed by Celite R or a commercial spill absorbant. After the absorbant containing the major share of the nitrosamine has been picked up (avoid dusts; do not sweep), the surface should be thoroughly cleaned with a strong detergent solution. If a major spill occurs outside of a ventilated area, the room should be evacuated, the OEHS Office (801-581-6590) should be contacted, and the cleanup operation should be carried out by persons equipped with self-contained respirators. Those involved in this operation should wear rubber gloves, laboratory coats, and plastic aprons or equivalent protective apparel.

• Nitrogen Dioxide (PHS). Nitrogen dioxide (NO2) is classified as a highly acute toxin; it is a primary irritant, acting principally on the lungs and to a lesser extent on the upper respiratory tract. It is certainly one of the most insidious of the gases. The inflammation of the lungs may cause only slight pain, but the edema that results may easily cause death. Toxic effects may develop after a 10 minute exposure to 10 ppm, and one hundred ppm of NO2 in air is a dangerous concentration for even a short exposure. Exposure to 200 ppm for 1-2 min may be fatal.

Nitrogen dioxide gas is reddish brown, has an irritating odor, and must be avoided by the use of an air-purifying respirator equipped with an acid-gas cartridge or canister; at concentrations greater than 50 times the TLV (threshold limit value), a positive-pressure atmosphere-supplying respirator must be used and, in IDLH atmospheres, a pressure-demand self-contained breathing apparatus or a positive-pressure air-line respirator that has escape-cylinder provisions is required.

Nitrogen dioxide is a deadly poison, and no one should work with a cylinder of this substance unless they are fully familiar with its handling and its toxic effect. Ventilation is extremely important, and respiratory protective equipment should always be available. Only stainless steel fittings should be used.

• **Perchlorates** should be avoided whenever possible. Perchlorate salts of organic, organometallic, and inorganic cations are potentially explosive and may detonate by heat or shock. Whenever possible, perchlorate should be replaced with safer anions such as fluoroborate, fluorophosphates, and trifluoromethanesulfonate (triflate).

Perchlorates should not be used as drying agents if there is a possibility of contact with organic compounds or of proximity to a dehydrating acid strong enough to concentrate the perchloric acid (HClO₄) (e.g., in a drying train that has a bubble counter containing sulfuric acid). Safer drying agents should be used.

Seventy percent 4 boils safely at approximately 200 °C, but contact of the boiling undiluted acid or the hot vapor with organic matter, or even easily oxidized inorganic matter, leads to serious explosions. Oxidizable substances must never be allowed to contact HClO4. This includes wooden benchtops or laboratory chemical hood enclosures, which may become highly flammable after absorbing HClO4 liquid or vapors. Beaker tongs, rather than rubber gloves, should be used when handling fuming HClO4. Perchloric acid evaporations should be carried out in a chemical hood that has a good draft.

The hood and ventilator ducts should be washed with water frequently (weekly; see PP) to avoid danger of spontaneous combustion or explosion if this acid is in common use.

- **Permanganates** are explosive when treated with sulfuric acid. If both compounds are used in an absorption train, an empty trap should be placed between them and monitored for entrapment.
- **Peroxides** (inorganic) should be handled carefully. When mixed with combustible materials, barium, sodium, and potassium peroxides form explosives that ignite easily.
- **Phenol** is a corrosive and moderately toxic substance that affects the central nervous system and can cause damage to the liver and kidneys. Phenol-formaldehyde reactions are used in creation of phenolic resins, and can be highly exothermic. These reactions have been implicated in a number of plant-scale accidents when runaway reactions caused a sudden rise in pressure and rupturing of pressure disks or vessels. Care should be taken if performing such reactions in the laboratory.

Phenol is readily absorbed through the skin and can cause severe burns to the skin and eyes. Phenol is irritating to the skin, but has a local anesthetic effect, so that no pain may be felt on initial contact. A whitening of the area of contact generally occurs and severe burns may develop hours after exposure. Exposure to phenol vapor can cause severe irritation of the eyes, nose, throat, and respiratory tract. In the event of skin exposure to phenol, do not immediately rinse the site with water. Instead, treat the site with low-

molecular-weight poly(ethylene glycol) (PEG) such as PEG 300 or PEG 400. This will safely deactivate phenol. Irrigate the site with PEG for at least 15 minutes or until there is no detectable odor of phenol.

- **Phosphorus** (P) (red and white) forms explosive mixtures with oxidizing agents. White phosphorus should be stored underwater because it ignites spontaneously in air. The reaction of phosphorus with aqueous hydroxides gives phosphine, which is toxic and also may either ignite spontaneously or explode in air.
- **Piranha solution** is a mixture of concentrated sulfuric acid and 30% hydrogen peroxide. It is a powerful oxidant and strong acid used to remove organic residues from various surfaces. Many instances of explosions have been reported with this solution upon contact with reducing agents, especially organics. The solution slowly evolves oxygen, and therefore containers must be vented at all times.
- **Potassium** (K) is much more reactive than sodium; it ignites quickly on exposure to humid air, and therefore should be handled under the surface of a hydrocarbon solvent such as mineral oil or toluene (see *Sodium*, below). Potassium can form a crust of the superoxide (KO₂) or the hydrated hydroxide (KOH·H2O) on contact with air. If this happens, the act of cutting a surface crust off the metal or of melting the encrusted metal can cause a severe explosion due to oxidation of the organic oil or solvent by superoxide, or from reaction of the potassium with water liberated from the hydrated hydroxide.
- Sodium (Na) should be stored in a closed container under kerosene, toluene, or mineral oil. Scraps of sodium or potassium should be destroyed by reaction with *n*-butyl alcohol. Contact with water should be avoided because sodium reacts violently with water to form hydrogen (H₂) with evolution of sufficient heat to cause ignition. Carbon dioxide, bicarbonate, and carbon tetrachloride fire extinguishers should not be used on alkali metal fires. Metals such as sodium become more reactive as the surface area of the particles increases. Prudence dictates using the largest particle size consistent with the task at hand. For example, use of sodium balls or cubes is preferable to use of sodium sand for drying solvents.
- Sodium amide (NaNH₂) can undergo oxidation on exposure to air to give sodium nitrite in a mixture that is unstable and may explode.
- Sodium Cyanide (and other cyanide salts) (PHS). Inorganic cyanide salts are classified as substances with a high degree of acute toxicity. Sodium cyanide is among the fastest acting of all known poisons. The lethal oral dose for humans is 200 mg. The symptoms of cyanide overdose include weakness, headache, confusion, and, occasionally, nausea and vomiting. Higher doses may be followed by almost instantaneous death. Solutions are irritating to the skin, nose, and eyes, and cyanide is absorbed through the skin. Sodium cyanide is highly toxic to animals via the oral route: LD50 (rats) = 6.4 mg/kg. It can be corrosive to the skin and the eyes, for it is highly alkaline. Sodium cyanide can also produce toxic symptoms via skin absorption and inhalation. The TLV (threshold limit value) and the OSHA PEL (permissible exposure limit) for cyanide are both 5 mg/m3 as an 8-hour

time-weighted average. These limits include a warning of the potential contribution of skin absorption to the overall exposure. In 1976, NIOSH recommended that the 5-mg/m₃ limit be retained but that its basis be changed from an 8-hour TWA to a 10-min ceiling.

Proper gloves should be worn when handling dry sodium cyanide. Rubber gloves and splash proof goggles should be worn when substantial amounts of sodium cyanide solution are used. Hydrolysis of sodium cyanide (and other cyanide salts) by water or acid generates HCN which is extremely hazardous. All reaction equipment in which cyanides are used or produced should be placed in or over shallow pans so that spills or leaks will be contained. In the event of spills of HCN or cyanide solutions, the contaminated area should be evacuated promptly and it should be determined immediately whether anyone had been exposed to cyanide vapors or liquid splash. Consideration should be given to the need for evacuating other parts of the building or notifying other occupants that the spill has occurred. In general, it is usually best not to attempt to dilute or absorb such spills if they occur in well-ventilated areas.

Detection – Hydrogen cyanide has a characteristic odor that resembles that of bitter almonds, however, many people cannot smell it in low concentrations, and this method of detection should not be relied on. Vapor-detector tubes sensitive to 1 ppm of HCN are available commercially. The presence of free cyanide ion in aqueous solution may be detected by treating an aliquot of the sample with ferrous sulfate and an excess of sulfuric acid. A precipitate of Prussian blue indicates that free cyanide ion is present.

Storage – Sodium cyanide and acids should not be stored or transported together. An open bottle of NaCN can generate HCN in humid air, and HCN may be liberated from spills of sodium cyanide solutions.

Waste disposal – Waste solutions containing cyanides should be sealed in clearly marked bottles. Contact the Environmental Management Office to arrange disposal of these containers.

In the event of exposure – Anyone who has been exposed to HCN should be removed from the contaminated atmosphere immediately. Any contaminated clothing should be removed and the affected area deluged with water. Emergency medical attention should be obtained immediately.

• Sulfuric acid (H₂SO₄) should be avoided, if possible, as a drying agent in desiccators. If it must be used, glass beads should be placed in it to help prevent splashing when the desiccator is moved. To dilute H₂SO₄, the acid should be added slowly to cold water. Addition of water to the denser H₂SO₄ can cause localized surface boiling and spattering on the operator.

F. Working with Cryogenics

Using cryogenic fluids improperly may produce physical and personal hazards that are not always obvious. The primary hazard to people is skin or eye contact with splashing liquid as it warms and expands. Injuries similar to a burn will result. Safety goggles or a face shield should be worn. Clean, insulated gloves that can *easily* be removed is suggested.

All cryogenic fluids are capable of causing asphyxiation without warning by displacing oxygen-containing air. Areas where they are used or stored should be adequately ventilated. These fluids should not be used in closed rooms or other enclosed spaces. Also, cryogenic fluids are capable of condensing oxygen from the air, causing oxygen enrichment or oxygen entrapment in confined spaces, which may result in increased flammability and subsequent explosion hazard.

Liquified gases are generally stored at atmospheric pressure in an insulated container, which keeps them near their boiling point, with some gas present. The large expansion in volume that takes place when the liquid becomes a gas means that pressure can build up in an unvented or unrelieved container and in transfer lines and piping. System design and maintenance must take this expansion ratio into account. Only containers designed for cryogenic fluids should be used. The selection of materials to be used with cryogenics is important because of the changes in physical properties of materials at very low temperatures. Some materials become extremely brittle. Chemical interactions between the cryogenic liquid and its container or equipment must also be evaluated.

The Dewar flask is the most common container used for storage and transfer of cryogenic fluids. When using the Dewar, follow these procedures.

- Cover the Dewar with a cap that allows escape of built-up pressure and keeps air and moisture out.
- Transfer cryogenic liquids from large Dewar vessels with special transfer tubes designed for the particular application.
- Tipping or tilting to pour the liquid may damage large Dewars.
- Do not use heat guns or similar equipment to warm transfer tubing quickly for disconnection.
- Handle containers carefully to protect the vacuum insulation system of Dewars.
- Place large Dewars on dollies that move freely so there is no possibility of personal injury or damage to the supported Dewars.

If there is a cryogenic spill, immediately leave the area. If you believe the cryogen has caused significant oxygen depletion, do not re-enter the area unless the oxygen content of the atmosphere is at least 19.5% and there is no flammable or toxic mixture present.

<u>Cold Traps</u>

- When using a cryogenic fluid in a Dewar for use on a vacuum line, it is imperative that the system be under vacuum when the Dewar is set in place.
- Only place dewars around traps after the system has been leak checked, and is under vacuum.
- Cold traps should be checked frequently/re-filled and not left unattended for extended periods of time.
- To remove dewars, isolate the traps from your line and vacuum, drop the dewars and vent the system. Place dewars in the back of a hood and allow trapped solvent to thaw.
- Important things to remember: never open a cold trap being cooled with a cryogen to the atmosphere as you will condense liquid oxygen.

Vacuum Transfers

Vacuum transfers and distillations often use cryogen cooled receiving flasks to increase the efficacy and speed of transfer. In order to prevent the condensation of liquid oxygen, take the following precautions:

- Verify that there are no leaks in the line (check the vacuum gauge / monometer). Never use a cryogen cooled receiving flask on a system with a leak.
- Monitor the pressure of the system under static vacuum leaks not only allow air to enter the system, but also slow the transfer of solvents.
- Never leave your vac transfer unattended for extended periods of time.

Emergency Procedures

In the event of a large cryogen spill, immediately leave the area until oxygen in the atmosphere is at least 19.5% in order to avoid asphyxiation hazards.

If you suspect your cold trap has condensed liquid oxygen, you (and everyone in your vicinity) are in immediate danger. Make sure that the hood sash is down, or that a blast shield is in front of the flask if the operation is not being performed in a hood.

- 1. Notify all lab occupants and your supervisor, and place a blast shield in front of the traps (even if in the hood).
- 2. Inspect the system, taking as many precautions as possible.

- 3. Try to ensure that the liquid nitrogen dewar in which the flask resides has ample liquid nitrogen in order to maintain a temperature of ~ -196 °C. This is to ensure that the Dewars are filled with plenty of cryogen to ensure the liquid oxygen is kept at an adequately low temperature. Warming of the liquid oxygen could result in pressure buildup and/or a violent oxidation reaction (if organics are present).
- 4. At this stage, you have several options:
 - a. Further venting the system to the open atmosphere is not advised, as this provides an ample supply of oxygen to the system, which may exacerbate the problem. If there are organics present, an explosion may result.
 - b. After ensuring that the dewar is filled with liquid nitrogen, try to locate the leak. If it can be fixed (as in a valve was left open, etc.), quickly seal the leak and put the system under dynamic vacuum (if not already so). If you cannot seal the leak effectively (such as if a valve broke), clear the area immediately and notify your supervisor. Do not re-enter the hood until the liquid oxygen has been pumped out of the cold trap (this may take several hours).
- 5. Your vacuum gauge/ monometer will indicate if you have fixed the leak and if liquid oxygen has been pumped off (changes by about 100 mm Hg). Evacuate the area. The entire system should be regarded as an explosive danger until no liquid oxygen remains (e.g., the vacuum is returned to its best reading).
- 6. Once the liquid oxygen is removed, get help from your advisor or another qualified researcher. Remove the dewar, then detach the flask from the line and allow it to warm slowly behind a blast shield.

If you suspect your cold trap has condensed liquid oxygen in the presence of an organic compound, the risk and extent of explosion is amplified. Follow the procedure outlined above, and notify the campus emergency service, at 4911. Absolutely ensure all lab occupants are evacuated, and that all entrances to the lab are closed off.

Appendix A: Departmental Chemical Hygiene Plan Completion Form

I,_____

(print full first and last name)

have read and agree to follow all of the safety rules described in the Department of Chemistry Chemical Hygiene Plan. I realize that I must obey these rules to insure my own safety, and the safety of those around me.

I realize that I must also complete the lab specific training outlined by my supervisor before beginning work in my laboratory.

I am aware that any violation of this contract that results in unsafe conduct in the laboratory or irresponsible behavior on my part, may result in dismissal from the laboratory and more serious consequences may result.

Signature:	Date:

PI Signature:_____ Date: _____

*Print a copy of this form, sign it, scan it, then upload the pdf into the Departmental Chemical Hygiene Plan Completion Form assignment on the Department of Chemistry Safety Canvas site. If you do not have access to a scanner you may try using using a smartphone app such as Genius Scan or Tiny Scanner.
Appendix B: Department of Chemistry SOP Templates

These templates are also found on the canvas safety site.

Department of Chemistry Special Chemical Assessment Form

Chemical: Attach any references on working with the particular chemical (eg, Aldrich Bulletins, MSDSs).

Name:	CAS #:	MW:
Formula:	Density:	Appearance:

Ratings of the Chemical (GHS, NFPA):

Hazards of the Chemical:

Corrosive	Flammable	Explosive
Oxidizer	Highly Flammable	Water Reactive
Reductant	Pyrophoric	Shock Sensitive
PHS	Poison	Other:

Personal Protective Equipment: Check all PPE needed during this reaction. Long pants, long sleeves, closed shoes, cotton lab coats, and safety glasses are always required.

Nomex Labcoat	Splash Goggles	Face Shield	
Nitrile Gloves	Butyl Gloves	Silver Shield Gloves	
Thermal Gloves	Thermal Gloves	Kevlar Gloves	
Kevlar Sleeves	Ear Protection	Other:	

What Engineering Controls Will be Required?

Fume Hood Bench Space:		Temperature Controllers	
Blast Shield Non-Flammable Bench Space		Pressure Regulators	
Other:	Other:	Other:	

Work Practice Controls:

Briefly explain what should be known/done when working with the chemical.

Transportation and Storage:

Briefly explain how the chemical should be stored (i.e., list incompatible chemicals and location of storage, container type, etc.)

Briefly note how the chemical should be transported (i.e., what kind of carrier to use when moving between labs, etc.)

What Chemicals and Equipment are Required to Deal with Possible Accidents?

What fire extinguisher will you need to put out flames?

How should spills be treated?

In the event of personal exposure, what steps should be taken (eg, should the safety shower be used)?

Other equipment required for accident mitigation:

How Will Waste be Handled? Are Special Waste Storage or Quenching Procedures Required?

Mention Anything Else You Think is Necessary.

Name:	Date:
Reviewer 1:	Date Reviewed:
Reviewer 2: (from another group)	Date Reviewed:

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Reviewer 3: (faculty)

Date Reviewed:

Department of Chemistry Special Reaction/Procedure Assessment Form

Chemical Reaction or Procedure:

Briefly describe your experiment and major hazards. Provide details below on any chemical reaction(s) that occur in your process. Show the species involved, the stoichiometry and the heat of reaction, if available. Also list side reactions and any other reactions that may impact safety. Attach any literature references for the procedure.

Hazards of the Chemicals Involved: Attach references or MSDSs if appropriate.

Corrosive	Flammable	Explosive
Oxidizer	Highly Flammable	Water Reactive
Reductant	Pyrophoric	Shock Sensitive
PHS	Poison	Other:

Experimental Conditions:

Temperature	Pressure	
Min:	Min:	
Max:	Max:	

Personal Protective Equipment: Check all PPE needed during this reaction. Long pants, long sleeves, closed shoes, cotton lab coats, and safety glasses are always required.

Nomex Labcoat Splash Goggles Face Shield		Face Shield
Nitrile Gloves	Butyl Gloves	Silver Shield Gloves
Thermal Gloves	Thermal Gloves	Kevlar Gloves
Kevlar Sleeves	Ear Protection	Other:

What Engineering Controls Will be Required?

Fume Hood Bench Space:		Temperature Controllers	
Blast Shield Non-Flammable Bench Space		Pressure Regulators	
Other:	Other:	Other:	

What Chemicals and Equipment are Required to Deal with Possible Accidents?

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What fire extinguisher will you need to put out flames?

How should spills be treated? What neutralization steps should be taken?

In the event of personal exposure, what steps should be taken (eg, should the safety shower be used)?

Other equipment required for accident mitigation:

How Will Waste be Handled? Are Special Waste Storage or Quenching Procedures Required?

Mention Anything Else You Think is Necessary.

Name:	Date:
Reviewer 1:	Date Reviewed:
Reviewer 2: (from another group)	Date Reviewed:
Reviewer 3: (faculty)	Date Reviewed:

Appendix C: Glove Compatibility Guide



This Chemical Resistance Guide incorporates three types of information:

- · Degradation (D) is a deleterious change in one or more of the glove's physical properties. The most obvious forms of degradation are the loss of the glove's strength and excessive swelling. Several published degradation lists (primarily "The General Chemical Resistance of Various Elastomers" by the Los Angeles Rubber Group, Inc.) were used to determine degradation.
- Breakthrough time (BT) is defined as the elapsed time between initial contact of the liquid chemical with the outside surface of the glove and the time at which the permeation rate reaches 0.1 mg/m^2 /sec. WHEN BREAKTHROUGH OCCURS, THE GLOVE IS NO LONGER PROVIDING ADEQUATE PROTECTION.
- · Permeation rate (PR), measured in milligrams per square meter per second (mg/m2/sec) is the meas-ured steady state flow of the permeating chemical through the glove elastomer. Glove thickness plays an important role in resistance to permeation.

The glove styles tested for permeation were the SSG, F101, B174, CS113B, LA102G and PNLB1815. The permeation data in this guide are based on permeation tests performed in accordance with ASTM Standard F 739 under laboratory conditions by North Safety Products or independent AHA accredited laboratories. Neither North Safety Products nor the independent laboratory assumes any responsibility for the suitability of an end user's selection of gloves based on this guide.

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CHEMICAL RESISTANCE GUIDE

(800) 430-4110. North also offers ezGuide", an interactive software program which is designed to electronically help you select the proper glove for use against specific chemicals. This "user friendly guide walks you step-by-step through the process to determine what type of glove to wear and its permeation resistance to the selected contaminant Product features, benefits and ordering information of the suggested products also are included in the program. ezGuide can be accessed from the North web site, www.northsafety.com or ordered by e-mailing us at marketing@northsafety.com

The finest chemical handling gloves deserve to be used with the finest respiratory products. Please consult the current North Safety Products Respiratory Protection Catalog and ezGuide" for proper respiratory selection.

Warning:

Protective gloves and other protective apparel selection must be based on the user's assessment of the workplace hazards. Glove and Apparel materials do not provide unlimited protection against all chemicals. It is the users responsibility to determine before use that the Glove and Apparel will resist permeation and degradation by the chemicals (including chemical mixtures) in the environment of intended use.

Failure by the user to select the correct protective gloves can result in injury, sickness or death

To obtain maximum life, protective gloves and other protective apparel should have chemicals removed from the surface by washing or other appropriate

Key to Degradation and Permeation Ratings

E - Excellent	Exposure has little or no effect. The glove retains its properties after extended exposure
G - Good	Exposure has minor effect with long term exposure. Short term exposure has little or no effect
F - Fair	Exposure causes moderate degradation of the glove. Glove is still useful after short term exposure but caution should be exercised with extended exposure
P - Poor	Short term exposure will result in moderate degradation to complete destruction
N/D	Permeation was not detected during the test
I/D	Insufficient data to make a recommendation

General Recommendation Color Key

Good	for	total	imm	orgion
0000	101	total		ersion

Good for accidental splash protection and intermittent contact

Only use with extreme caution. Glove will fail with only short exposure

Physical Performance Chart

Physical Characteristics	Silver Shield®	Vitoe*	Betyl	Chemsoft [®]	Nitrile	Natural Rubber
Abrasion Resistance	F	G	G	E	E	E
Cut Resistance	Р	G	G	E	E	E
Puncture (Snag) Resistance	P	G	G	E	E	E
Flexibility	E	G	G	E	E	E
Heat Resistance	F	6	6	G	6	6

		oni uie si	unace by w	rashing o	ouler ap	propriate		(CO	INCOLORED.	c		· · · ·							
		S	ilver Shie	ble		Viton			Butyl		(Chemsof	t		Nitrile		Nat	ural Rub	ber
Chemical Name	CAS No.	D	BT	PR	D	BT	PR	D	BT	PR	D	BT	PR	D	BT	PR	D	BT	PF
Diethyl Oxide	60-29-7	E	>8 hrs	N/D	р	12 min	21.5	Р	8 min	92.2	νo	ψD	VD	Р	14 min	21.8	VD	VD	1/0
Diethylamine	109-89-7	E	>8 hrs	N/D	Р	35 min	852	Р	47 min	46	VD.	U/D	VD	F	U/D	I/D	VD	VD	I/I
Diethylaminoethanol	100-37-8	I/D	U/D	U/D	E	>8 hrs	N/D	E	>8 hrs	N/D	E	>7.8 hrs	0.02	E	>8 hrs	N/D	VD.	VD	Ņ
1,4-Diethylene Dioxide	123-91-1	I/D	1/D	U/D	Р	23 min	26.8	E	>20 hrs	N/D	UD.	U/D	VD.	Р	28 min	77.4	VD.	VD	V
Diethylene Ether	123-91-1	I/D	U/D	U/D	Р	23 min	26.8	E	>20 hrs	N/D	VD	U/D	VD	Р	28 min	77.1	VD	VD	V
Diethylene Oxide	123-91-1	I/D	VD.	U/D	Р	23 min	26.8	E	>20 hrs	N/D	VD	U/D	VD	Р	28 min	77.4	VD	VD	V
Diethylenetriamine	111-40-0	I/D	VD.	U/D	E	>8 hrs	N/D	E	>8 hrs	N/D	VD	UD.	VD	Р	U/D	I/D	VD	VD	V
Disobutyl Ketone (80%)	108-83-8	E	>8 hrs	N/D	F	1.1 hrs	90.6	G	3.3 hrs	41.2	VD	VD	VD	F	2.9 hrs	49	VD	VD	Ų
Dimethyl Acetamide	127-19-5	F	1.5 hrs	0.728	Р	25 min	3	E	>8 hrs	N/D	UD.	UD.	I/D	1/0	U/D	I/D	Ų۵	UD.	Ų
Dimethyl Formamide	68-12-2	E	>8 hrs	N/D	Р	8 min	6.5	E	>8 hrs	N/D	UD.	U/D	1/D	F	9 min	15	VD.	(VD	- V
Dimethyl Mercury	593-74-8	E	>4 hrs	<0.017	Р	<15 min	3.1	Р	<15 min	46.7	VD	U/D	ŲD.	I/D	U/D	I/D	VD.	VD	V
Dimethyl Sulfoxide	67-68-5	G	U/D	U/D	F	1.5 hrs	5	E	>8 hrs	N/D	F	41 min	3.7	F	40 min	5.2	VD	VD	V
Dimethylketone	67-64-1	E	>8 hrs	N/D	Р	2 min	383	E	>8 hrs	N/D	Р	1 min	42.3	Р	3 min	291	Р	10 min	12
Dioctyl Phthalate	117-81-7	I/D	1/D	U/D	E	>8 hrs	N/D	E	>8 hrs	N/D	E	>8 hrs	N/D	E	>8 hrs	N/D	VD	VD	ų
1,4-Dioxane	123-91-1	I/D	1/D	U/D	Р	23 min	26.8	E	>20 hrs	N/D	UD.	UD.	VD	Р	28 min	77.4	VD.	VD	Ų
Dioxyethylene Ether	123-91-1	I/D	1/D	U/D	Р	23 min	26.8	E	>20 hrs	N/D	U/D	U/D	1/D	Р	28 min	77.4	VD.	(VD	Ų
Divinyl Benzene	1321-74-0	E	>8 hrs	N/D	E	>17 hrs	N/D	F	2.2 hrs	238	VD.	U/D	VD	Р	VD.	I/D	VD	VD	Ų
Epichlorohydrin	106-89-8	I/D	U/D	U/D	Р	2 hrs	4	E	>8 hrs	N/D	UD.	U/D	UD.	Р	U/D	I/D	VD.	VD	ų
1,2-Epoxypropane	75-56-9	I/D	U/D	U/D	Р	1 min	1790	F	2.2 hrs	7	VD.	UD.	VD	Р	<6 min	>3.9	VD	VD	Ų
Ethanal	75-7-0	E	>8 hrs	N/D	Р	0 min	281.9	E	>8 hrs	0.066	VD	U/D	VD	P	0 min	161	VD	VD	ų
Ethanol	64-17-5	E	>8 hrs	N/D	VD	I/D	(/D	E	>8 hrs	N/D	F	1.2 hrs	3.3	I/D	I/D	I/D	VD.	VD	Ų
Ether	60-29-7	E	>8 hrs	N/D	Р	12 min	21.5	Р	8 min	92.2	UD.	U/D	1/D	Р	14 min	21.8	VD.	(VD	Ų
Ethyl Acetate	141-78-6	E	>8 hrs	N/D	Р	VD	VD	G	7.6 hrs	3.4	VD	U/D	VD	Р	8 min	145	VD	VD	Ų
Ethyl Alcohol	64-17-5	E	>8 hrs	N/D	VD	U/D	VD	E	>8 hrs	N/D	F	1.2 hrs	3.3	1/0	U/D	I/D	G	31 min	Z
Ethyl Aldehyde	75-07-0	E	>8 hrs	N/D	р	0 min	281.9	E	>8 hrs	0.066	VD.	U/D	UD.	Р	0 min	161	VD	VD	V
Ethyl Ether	60-29-7	E	>8 hrs	N/D	Р	12 min	21.5	Р	8 min	92.2	νD	VD	1/D	Р	14 min	21.8	VD	UD.	ų
Ethylamine (70% in water)	75-04-7	F	51 min	0.65	Р	I/D	U/D	E	>12 hrs	N/D	UD.	U/D	1/D	F	1.1 hrs	30.1	VD.	(VD	Ų
Ethylene Dichloride	107-06-2	E	>8 hrs	N/D	E	>8 hrs	N/D	F	2.9 hrs	53	U/D	UD.	1/D	Р	8 min	82.7	VD.	UD.	Ļ
Ethylene Glycol	107-21-1	I/D	1/D	UD.	VD	1/D	VD	VD.	U/D	(/D	E	>8 hrs	N/D	1/0	U/D	I/D	E	>8hrs	N
Ethylene Oxide	75-21-8	E	>8 hrs	N/D	E	>8 hrs	N/D	E	>8 hrs	N/D	UD.	U/D	VD	1/0	U/D	I/D	VD	VD	Ų
Formaldehyde (37% in water)	50-00-0	E	>8 hrs	N/D	E	>16 hrs	N/D	E	>16 hrs	N/D	E	>8hrs	0.007	E	>21 hrs	N/D	VD	VD	I
Furfural	98-01-1	E	>8 hrs	N/D	F	3.5 hrs	14.8	E	>16 hrs	N/D	U/D	UD.	1/D	P	24 min	265	VD	I/D	I
Glutaraldehyde (25%)	111-30-8	I/D	1/D	U/D	E	>8 hrs	N/D	E	>8 hrs	N/D	U/D	U/D	U/D	P	L/D	I/D	E	>6 hrs	N
Heptane	142-82-5	I/D	U/D	U/D	UD	I/D	VD	I/D	U/D	(/D	E	>6 hrs	N/D	I/D	U/D	I/D	VD	UD.	Ų
Hexahydrobenzene	110-82-7	E	>4hrs	N/D	E	>7 hrs	N/D	F	50 min	103.8	E	>8 hrs	N/D	F	U/D	I/D	VD	VD	V

		Si	ilver Shie	ble		Viton			Butyl		(Chemsof	t	Nitrile			Natural Rubber		
Chemical Name	CAS No.	D	BT	PR	D	BT	PR	D	BT	PR	D	BT	PR	D	BT	PR	D	BT	PR
Hexahydrophenol	108-93-0	E	>8 hrs	N/D	E	>8 hrs	N/D	E	>ff hrs	N/D	E	>6 hrs	N/D	E	>16 hrs	N/D	VD	VD	1/0
Hexamethylene	110-82-7	E	>4hrs	N/D	E	>7 hrs	N/D	F	50 min	103.8	E	>8 hrs	N/D	F	VD	I/D	VD.	VD	I/D
Hexanaphthene	110-82-7	E	>4hrs	N/D	E	>7 hrs	N/D	F	50 min	103.8	E	>8 hrs	N/D	F	UD.	I/D	1/D	(VD	I/D
Hexane	110-54-3	E	>8 hrs	N/D	E	>8 hrs	N/D	Р	U/D	I/D	E	>6 hrs	N/D	E	U/D	I/D	1/D	U/D	I/D
Hydrochloric Acid (37%)	7647-01-0	E	>8 hrs	N/D	E	VD.	VD	E	VD	U/D	E	>6 hrs	N/D	E	>6 hrs	N/D	E	>6 hrs	N/D
Hydrofluoric Acid (48%)	7664-39-3	E	>8 hrs	0.013	G	ŲD.	VD	F	VD	1/D	vo	UD.	ŲD	G	1 hr	0.49	E	7 hrs	0.18
Hydrogen Chloride (gas)	7647-01-0	E	>8 hrs	N/D	E	>8 hrs	N/D	E	>8 hrs	N/D	VD.	UD.	ŲD	1/0	UD.	I/D	VD.	VD	I/D
lodomethane	74-88-4	Р	4 min	0.026	E	6.3 hrs	0.7	F	55 min	82	VD	UD.	VD	I/D	VD.	I/D	VD.	VD	I/D
Isobutyl Alcohol	78-83-1	E	U/D	U/D	E	>8 hrs	N/D	E	>8 hrs	N/D	E	>8 hrs	N/D	E	>8 hrs	N/D	1/D	U/D	I/D
Isopropyl Alcohol	67-63-0	I/D	U/D	U/D	VD	U/D	U/D	UD.	U/D	I/D	E	>6 hrs	N/D	E	>6 hrs	N/D	G	1.7 hrs	0.42
Ketohesamethylene	108-94-1	E	>8 hrs	N/D	Р	29 min	86.3	E	>16 hrs	N/D	vo	UD.	VD	Р	VD	I/D	F	2.1 hrs	0.07
Methacrylic Acid	79-41-4	I/D	VD.	UD.	E	>8 hrs	N/D	E	>8 hrs	N/D	VD.	UD.	νD	F	1.7 hrs	Z3	VD	VD	1/0
Methacrylonitrile	126-98-7	E	U/D	ιø	F	4 min	462	E	>8 hrs	N/D	vo	U/D	VD	P	7 min	560	VD.	VD	I/D
Methanol	67-56-1	E	6 hrs	0.02	F	3 hrs	1	E	>8 hrs	N/D	UD.	U/D	VD	F	32 min	11.8	F	19 min	1.97
Methenyl Trichloride	67-66-3	E	>8 hrs	N/D	E	9.5 hrs	0.46	٧D	UD.	I/D	U/D	UD.	ŲD	P	4 min	352	1/D	(VD	I/D
Methyl Alcohol	67-56-1	E	6 hrs	0.02	F	3 hrs	- 1	E	>8 hrs	N/D	UD.	U/D	ŲD	F	32 min	11.8	F	19 min	1.97
1-Methyl-4-tert-butylbenzene	98-51-1	E	>8 hrs	N/D	E	>8 hrs	N/D	F	1.78 hrs	8	UD.	UD.	ų۵	Р	VD	I/D	VD	VD	1/D
Methyl Cellosolve	109-86-4	I/D	U/D	(/D	VD	U/D	VD	VD	U/D	1/D	UD.	U/D	ŲD	F	55 min	13.2	F	45 min	0.56
Methyl Chloride	74-87-3	E	>8 hrs	N/D	E	>8 hrs	N/D	E	>8 hrs	N/D	E	>8 hrs	0.0013	I/D	VD.	I/D	VD	VD	I/D
Methyl Chloroform	71-55-6	E	>8 hrs	N/D	E	>15 hrs	N/D	Р	U/D	I/D	UD.	UD.	VD	Р	37 min	76.4	VD.	VD	I/D
Methyl lodide	74-88-4	Р	4 min	0.026	E	6.3 hrs	0.7	F	55 min	82	UD.	UD.	UD.	I/D	VD.	I/D	1/D	VD	I/D
Methylamine (40% in water)	74-89-5	F	46 min	1.28	E	>16 hrs	N/D	E	>15 hrs	N/D	F	1.7 hr	7	E	>8 hrs	N/D	VD.	VD	I/D
Methylbenzene	108-88-3	E	>8 hrs	N/D	E	>16 hrs	N/D	Р	6 min	511	νD	UD.	ŲD	р	11 min	68.1	Р	3 min	82.2
Methylene Chloride	75-09-2	E	>8 hrs	N/D	F	1 hr	7.32	Р	VD	VD	Р	UD.	ŲD	Р	4 min	766	VD.	VD	I/D
4,4-Methylene Dianiline	101-77-9	E	>8 hrs	N/D	E	>8 hrs	N/D	E	>8 hrs	N/D	VD.	UD.	VD	F	VD	I/D	VD	VD	I/D
Monoethanolamine	141-43-5	I/D	1/D	U/D	E	>8 hrs	N/D	E	>8 hrs	N/D	E	>8 hrs	N/D	I/D	VD.	I/D	VD.	(/D	I/D
Morpholine	110-91-8	E	>8 hrs	N/D	G	1.9 hrs	97	E	>16 hrs	N/D	UD.	U/D	UD	Р	48 min	206	1/D	U/D	I/D
Naphtha	8052-41-3	E	>8 hrs	N/D	VD	1/D	1/D	VD	U/D	1/D	E	>8 hrs	N/D	E	>6 hrs	N/D	VD.	(VD	I/D
n-Hexane	110-54-3	E	>8 hrs	N/D	E	>8 hrs	N/D	ψD	U/D	(/D	E	>6 hrs	N/D	I/D	VD	I/D	ŲD.	VD	I/D
Nitrobenzene	98-95-3	E	>8 hrs	N/D	E	>8 hrs	N/D	E	>8 hrs	N/D	ŲΟ	U/D	VD	F	29 min	1.7	P	7 min	8.4
Nitromethane	75-52-5	I/D	VD	ŲΟ	VD	VD	VD.	E	>8 hrs	N/D	VD.	UD.	ŲD	I/D	VD	I/D	P	7 min	2.83
1-Nitropropane	108-03-2	E	>8 hrs	N/D	Р	17 min	26.1	E	>8 hrs	N/D	ŲΟ	U/D	VD	Р	12 min	29.5	1/D	VD	I/D
n-Methyl-2-Pyrrolidone	872-50-4	I/D	VD.	U/D	VD	VD.	U/D	E	8 hrs	N/D	U/D	U/D	VD	F	1.45 hrs	0.388	F	1.26 hrs	3.14
n-Propyl Acetate	109-60-4	E	>8 hrs	N/D	VD	VD.	U/D	F	2.7 hrs	2.86	U/D	U/D	(VD	P	17 min	72.5	1/D	U/D	I/D
Oxalic Acid	144-62-7	E	>8 hrs	N/D	E	>8 hrs	N/D	E	>8 hrs	N/D	U/D	VD	VD	G	1/D	I/D	VD	U/D	VD/
D = Degradation BT = Breakthrough Time PR = Permeation Rate	E = Excel G = Good F = Fair	lent	N/D = I/D =	None Insuff	Detected ficient Da	ta						Good	i for total i for acci	i immersio dentai spi	on ash protec	ction and	Intermitte	ent contac	t
	P = Poor											Only	use with	extreme	caution. G	Giove will	fall with	only short	exposure

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		Si	ilver Shi	ble		Viton			Butyl		(Chemsof	t		Nitrile		Nat	ural Rub	ber
Chemical Name	CAS No.	D	BT	PR	D	BT	PR	D	BT	PR	D	BT	PR	D	BT	PR	D	BT	PR
p-Dioxane	123-91-1	I/D	VD	vo	р	23 min	26.8	E	>20 hrs	N/D	vo	νo	vo	р	28 min	77.1	νD	VD	I/D
Perchloric Acid (70%)	7601-90-3	I/D	VD.	U/D	VD	VD.	VD	VD	VD	VD	E	>8 hrs	N/D	E	>8 hrs	N/D	VD	VD	I/D
Perchloroethylene	127-18-4	E	>8 hrs	N/D	E	>17 hrs	N/D	Р	VD.	ŲD.	F	1 hr	3.8	F	1.3 hrs	5.5	VD	VD	I/D
Perchloromethane	56-23-5	E	>8 hrs	N/D	E	>13 hrs	N/D	ŲD	U/D	1/D	F	1.3 hrs	3.45	F	3.4 hrs	5	VD	VD	I/D
Phenol (85% in water)	108-95-2	E	>8 hrs	N/D	E	>15 hrs	N/D	E	>20 hrs	N/D	VD	U/D	ŲD	Р	39 min	>1500	F	2.2 hrs	4.64
Phenylamine	62-53-3	E	>8 hrs	N/D	Р	6 min	18.7	E	>8 hrs	N/D	UD.	U/D	VD	F	1.1 hrs	45	VD	VD	I/D
Phosphoric Acid (85%)	7664-38-2	I/D	VD.	(/D	VD	VD.	VD	VD	VD.	VD	E	>8 hrs	N/D	E	>8 hrs	N/D	E	>8 hrs	N/D
Pimelic Ketone	108-94-1	E	>8 hrs	N/D	Р	29 min	86.3	E	>16 hrs	N/D	UD.	U/D	VD	I/D	VD.	I/D	F	2.1 hrs	0.07
2-Propanone	67-64-1	E	>8 hrs	N/D	Р	2 min	383	E	>8 hrs	N/D	Р	1 min	42.3	Р	3 min	291	Р	10 min	12.2
Propyl Acetate	109-60-4	E	>8 hrs	N/D	Р	U/D	VD	G	2.7 hrs	2.86	VD	UD.	VD	Р	17 min	72.5	VD	VD	I/D
Propyl Alcohol	71-23-8	I/D	U/D	U/D	VD	U/D	1/D	٧D	U/D	U/D	G	3.8 hrs	0.35	E	4.4 hrs	4.4	V D	VD	I/D
Propylene Oxide	75-56-9	I/D	VD.	(/D	Р	1 min	1790	F	2.2 hrs	7	VD	UD.	ŲD	Р	<6 min	>3.9	ŲD	VD	I/D
p-tert-Butyltoluene	98-51-1	E	>8 hrs	N/D	E	>8 hrs	N/D	F	1.78 hrs	8	VD	U/D	VD	Р	UD.	I/D	VD	VD	I/D
Pyridine	110-86-1	I/D	VD.	(/D	Р	38 min	74	E	>8 hrs	N/D	VD	VD	VD	Р	UD.	I/D	VD	VD	I/D
Sodium Hydroxide 50%	1310-73-2	E	>8 hrs	N/D	E	>8 hrs	N/D	E	>8 hrs	N/D	E	>8 hrs	N/D	E	>8 hrs	N/D	E	>8 hrs	N/D
Stoddard Solvent	8052-41-3	E	>8 hrs	N/D	VD	U/D	VD.	ψD	VD	ŲD	E	>8 hrs	N/D	E	>6 hrs	N/D	ŲD	VD	I/D
Styrene	100-42-5	E	>6 hrs	N/D	E	>6 hrs	N/D	F	35 Mins	0.19	Р	16 min	39	Р	11 min	>3.35	VD	VD	I/D
Sulfuric Acid (50%)	7664-93-9	E	>6 hrs	N/D	E	U/D	VD	E	VD	VD.	G	>8 hrs	N/D	G	>6 hrs	N/D	G	>6 hrs	N/D
Sulfuric Acid (93%)	7664-93-9	E	>8 hrs	N/D	E	>8 hrs	N/D	E	>8 hrs	N/D	Р	2 min	N/D	F	1.9 hrs	11.4	G	5.1 hrs	N/D
Tetrachloroethylene	127-18-4	E	>8 hrs	N/D	E	>17 hrs	N/D	Р	VD	VD.	F	1 hr	3.8	F	1.3 hrs	5.5	VD	VD	I/D
Tetrachloromethane	56-23-5	E	>8 hrs	N/D	E	>13 hrs	N/D	VD	VD.	VD	F	1.3 hrs	3.45	F	3.4 hrs	5	VD	VD	I/D
Tetrahydrofuran	109-99-9	E	>8 hrs	N/D	Р	0 min	327	F	27 min	112	Р	VD	VD	Р	0 min	167	Р	5 min	360
Thioglycolic Acid	68-11-1	I/D	U/D	U/D	E	>8 hrs	N/D	E	>8 hrs	N/D	VD	U/D	VD	I/D	VD	I/D	VD	VD	I/D
Toluene	108-88-3	E	>8 hrs	N/D	E	>16 hrs	N/D	Р	6 min	511	Р	VD.	VD	Р	11 min	68.1	Р	3 min	82.2
Toluene Diisocyanate	584-84-9	E	>8 hrs	N/D	VD	U/D	VD	E	VD	1/D	F	1 hr	2.52	G	UD.	I/D	VD	VD	I/D
1,1,1-Trichloroethane	71-55-6	E	>8 hrs	N/D	E	>15 hrs	N/D	Р	VD	VD	VD	VD	VD	F	37 min	76.4	VD	VD	I/D
Trichloroethylene	79-01-6	E	>8 hrs	N/D	E	7.4 hrs	0.24	Р	14 min	550	UD.	UD.	VD	Р	4 min	283	Р	<5 min	894
Trichloromethane	67-66-3	E	>8 hrs	N/D	E	9.5 hrs	0.46	VD	U/D	VD	U/D	VD	VD	Р	4 min	352	VD	VD	I/D
Triethanolamine	102-71-6	I/D	VD.	VD	VD	U/D	VD	E	>8 hrs	N/D	E	>8 hrs	N/D	I/D	VD	I/D	E	>8 hrs	N/D
Triethylamine	121-44-8	I/D	VD.	VD.	E	>8 hrs	N/D	Р	VD	VD	E	5.8 hrs	0.18	E	>8 hrs	N/D	VD	VD	I/D
Vinegar Naphtha	141-78-6	E	>8 hrs	N/D	Р	ŲD.	VD	E	7.6 hrs	3.4	U/D	U/D	VD	P	8 min	145	VD	VD	I/D
Vinylstyrene	1321-74-0	E	>8 hrs	N/D	E	>17 hrs	N/D	F	2.2 hrs	238	U/D	U/D	VD	Р	ŲD	I/D	VD	VD	I/D
Xylene	1330-20-7	E	>8 hrs	N/D	E	>8 hrs	N/D	Р	VD	VD	Р	U/D	VD	Р	21 min	18.5	VD	VD	I/D
D = Degradation	E = Excel	lent	N/D =	None	Detected							Good	i for total	Immersio	m				

BT = Breakthrough Tim PR = Permeation Rate

G = Good F = Fair P = Poor

Good for accidental splash protection and intermit ent co ct

Only use with extreme caution. Glove will fail with only short expo

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Viton[®] - Unsupported Gloves

Excellent chemical resistance to chlorinated and aromatic solverits. Can be used in water based solvents without dissolving. Superior resistance to PCBs. Curved finger and hand design provides better fit for greater worker comfort.

Vilon[®] is a registered trademark of the DuPont company.



Part No.	Description	Sizes	Grip/Cuff	Length/Gauge	Inner Pack	Case Pack
F101	Black, sanitized interior	8-11	Smooth/straight	11"/10 mil	1 pair	10 pair
F124	Black, sanitized interior	8-11	Smooth/straight	14"/12 mil	1 pair	10 pair

Silver Shield®/4H® Gloves

Resistant to over 280 different chemicals: alcohols, alightatic, aromatics, chlorines, lectones, esters. Low cost, disposable gioves don thave to be resyled and can be readily available to workers. Does not contain chemical accelerators that can cause allergic reactions. Can be used as a secondary inner glove. Allows worker maximum protection in heavy-daty jobs where the dangers of mechanical damage to gloves are high.

Part No.	Description	Sizes	Grip/Cuff	Length/Gauge	Inner Pack	Case Pack
SSG	Silver, unlined	6, 7, 8	Smooth/straight	14.5"/2.7 mil	10 pair	50 pair
		9, 10, 11	Smooth/straight	16"/2.7 mil	10 pair	50 pair
SSG29/10	Silver, unlined	10	Smooth/straight	29"/2.7 mil	10 pair	50 pair

NitriGuard Unsupported Nitrile Gloves

100% nitrile content offers superior resistance to cuts, snags, abrasions and punctures. Gloves are free of lates proteins which can cause allergic reactions. Comply with USDA and FDA regulations, 21 CFR, for use in food processing. Available with unlined or Blocket interior.

Part No.	Description	Sizes	Grip/Cuff	Length/Gauge	Inner Pack	Case Pack
LA102G	Green, sanitized interior	7-11	Sandpatch/straight	13"/11 mil	1 dz pair	12 dz pair
LA142G	Green, sanitized interior	7-11	Sandpatch/straight	13"/15 mil	1 dz pair	12 dz pair
LA225G	Green, sanitized interior	7-11	Sandpatch/straight	15"/22 mil	1 dz pair	6 dz pair
LA258G	Green, sanitized interior	7-11	Sandpatch/straight	18"/25 mil	1 dz pair	6 dz pair
LATTIEB	Blue, sanitized interior	7-11	Sandpatch/straight	13"/11 mil	1 dz pair	12 dz pair
LA132G	Green, flock interior	7-11	Sandpatch/straight	13"/15 mil	1 dz pair	12 dz pair
LA172G	Green, flock interior	7-11	Sandpatch/straight	13"/17 mil	1 dz pair	12 dz pair
LATTTEBFL	Blue, flock interior	7-11	Sandpatch/straight	13"/15 mil	1 dz pair	12 dz pair

Butyl - Unsupported Gloves

Highest permeation resistance to gas and water vapor for greater worker protection, especially when handling toxic substances. Flexible and sensitive, even at lower temperatures. Curved finger and hand design provides a better fit for greater worker comfort. Available with "Grip-Saf" palm for wet applications.

Part No.	Description	Sizes	Grip/Cuff	Length/Gauge	Inner Pack	Case Pack	
8131	Black, sanitized interior	7-11	Smooth/rolled bead	11"/13 mil	1 pair	288 pair	
B131R	Black, sanitized interior	7-11	Rough Grip-Sat/rolled beau	d 11"/13 mil	1 pair	288 pair	
B161	Black, sanitized interior	7-11	Smooth/rolled bead	11"/16 mil	1 pair	144 pair	
B161R	Black, sanitized interior	7-11	Rough Grip-Sat/rolled bear	d 11"/16mil	1 pair	72 pair	
B174	Black, sanitized interior	7-11	Smooth/rolled bead	14"/17 mil	1 pair	288 pair	
B174R	Black, sanitized interior	7-11	Rough Grip-Saf/rolled bear	d 14"/17 mil	1 pair	288 pair	
8324	Black, sanitized interior	7-11	Smooth/rolled bead	14"/32 mil	1 pair	144 pair	
8324R	Black, sanitized interior	7-11	Rough Grip-Sat/rolled beau	d 14"/32 mil	1 pair	72 pair	
90746	Black, sanitized interior	XS- XL	Smooth/rolled bead	14"/7 mil	1 pair	100 pair	
9074RG	Black, sanitized interior	XS-XL	Rough/rolled bead	14°/7 mil	1 pair	100 pair	
8144G	Black, sanitized interior	XS- XL	Smooth/rolled bead	14"/14 mil	1 pair	100 pair	
B144RG	Black, sanitized interior	XS- XL	Rough/rolled bead	14"/14 mil	1 pair	100 pair	
81749	Black, sanitized interior	XS- X1	Smooth/rolled bead	14"/17 mil	1 pair	100 pair	
8174RG	Black, sanitized interior	XS- XL	Rough/rolled bead	14"/17 mil	1 pair	100 pair	
9254G	Black, sanitized interior	XS- XL	Smooth/rolled bead	14"/25 mil	1 pair	100 pair	
254RG	Black, sanitized interior	XS- XL	Rough/rolled bead	14"/25 mil	1 pair	100 pair	
20.000	Black and Stand School and Black	VC VI	County for Bad band	14100	d min	400	

Chemsoft®Industrial Glove

Unique patented 100% nitrile formulation is 59% stretchier' than the leading industrial weight nitrile gloves. Gives warer desterily required to pick up small parts, better than comparable nitrile gloves on the market, without hand fatigue. Comply with USUA and FDA regulations, 21 CFR, for use in food processing. Free of lates proteins which can cause allergic reactions.

" Banel on an independent scientific companion between the new North Chemoth Industrial gives and Anell-Edmont Sof-Vac brand conducted by the Aron Riddor Development Laboratory

Part No.	Description	Sizes	Grip/Cuff	Length/Gauge	Inner Pack	Case Pack
CS113B	Blue, sanitized interior	7-11	Sandpatch/straight	13"/11 mil	1 dz pair	12 dz pair
CS153B	Black, flock interior	7-11	Sandpatch/straight	13"/15 mil	1 dz pair	12 dz pair

Unsupported Premium Natural Rubber*

100% high natural rubber has excellent desterity, elasticity, and tensile strength for long wear and comfort. Embossed palm and fingers have a better wet grip. Rolled edge prevents cuff from tearing. Obiornated for more comfort and ease when using. Complex with USU and FDA regulations, 21 CFR, for use in food processing. "CUTION The prodet centers nature other late present which may crase along's matters.

Part No.	Description	Sizes	Grip/Cuff	Length/Gauge	Inner Pack	Case Pack
PNLB1815	Orange, sanitized interior	7-11	Diamond embossed/bead	15"/18 mil	1 dz pair	12 dz pair





Appendix D: Qualitative Test for Fume hood Performance

Taken from PP.

BOX 6.1 A Simple Qualitative Method to Verify Adequate Laboratory Chemical Hood Ventilation

Materials

- 200 g (approximately 250 mL) of dry ice pellets (5to 10-mm diam)
- Shallow bowl, approximately 3-L volume
- 1 L water at 43 °C (mix hot and cold water as needed to obtain the target temperature) Thermometer

Procedure

- 1. Open the chemical fume hood sash to simulate actual operation. Position laboratory equipment as close as possible to where it will be used.
- 2. Place the shallow bowl approximately 15 cm into the chemical fume hood and in the center of the sash opening.
- 3. Add 1 L of the warm water to the bowl.
- 4. Add the dry ice pellets to the water.
- 5. After approximately 5 s, observe the vapor flowing from the bowl.
- 6. Repeat the observation while a colleague walks past or moves around the chemical fume hood to simulate actual operation.
- 7. If vapors are observed escaping the chemical fume hood face, the result is a fail; none escaping is a pass.

In the event of a failure or if there is any concern about proper operation, contact appropriate personnel and take corrective action. Adjustment of the sash opening and the baffles and relocation of equipment in the chemical fume hood should be considered.

NOTE: In addition, airflow should be measured on an annual basis.

Appendix E: Table of Fire Hazard Ratings from Prudent Practices

	NFPA Flammability	Flash Point	Boiling Point	Ignition Temperature	Flammable Lim (% by volume)	its
	Rating ^a	(°C)	(°C)	(°C)	Lower	Upper
Acetaldehyde	4	-39	21	175	4	60
Acetic acid (glacial)	2	39	118	463	4	19.9
Acetone	3	-20	56	465	2.5	12.8
Acetonitrile	3	6	82	524	3	16
Carbon disulfide	4	-30	46	90	1.3	50
Cyclohexane	3	-20	82	245	1.3	8
Diethylamine	3	-23	57	312	1.8	10.1
Diethyl ether	4	-45	35	180	1.9	36
Dimethyl sulfoxide	2	95	189	215	2.6	42
Ethyl alcohol	3	13	78	363	3.3	19
Heptane	3	-4	98	204	1.05	6.7
Hexane	3	-22	69	225	1.1	7.5
Hydrogen	4		-252	500	4	75
Isopropyl alcohol	3	12	83	399	2	12.7 @ 200 (93)
Methyl alcohol	3	11	64	464	6	36
Methyl ethyl ketone	3	-9	80	404	1.4 @ 200 (93)	11.4 @ 200 (93)
Pentane	4	<-40	36	260	1.5	7.8
Styrene	3	31	146	490	0.9	6.8
Tetrahydrofuran	3	-14	66	321	2	11.8
Toluene	3	4	111	480	1.1	7.1
p-Xylene	3	25	138	528	1.1	7

TABLE 4.4NFPA Fire Hazard Ratings, Flash Points (FP), Boiling Points (bp), IgnitionTemperatures, and Flammable Limits of Some Common Laboratory Chemicals

^{*a*}0, will not burn under typical fire conditions; 1, must be preheated to burn, liquids with FP \geq 93.4 °C (200 °F); 2, ignitable when moderately heated, liquids with FP between 37.8 °C (100 °F) and 93.4 °C (200 °F); 3, ignitable at ambient temperature, liquids with FP < 22.8 °C (73 °F), bp \geq 37.8 °C (100 °F) or FP between 22.8 °C and 37.8 °C (100 °F); 4, extremely flammable, readily dispersed in air, and burns readily, liquids with FP < 22.8 °C (73 °F), bp < 37.8 °C (100 °F). SOURCE: Adapted with permission from *Fire Guide to Hazardous Materials* (13th Edition), Copyright © 2001, National Fire Protection Association.

Appendix F: Partial List of Chemical Incompatibility

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CHEMICAL	INCOMPATIBILITY
Acetic acid	Chromic acid, nitric acid, hydroxyl compounds, ethylene glycol,
	perchloricacid, peroxides, permanganates
Acetone	Concentrated nitric and sulfuric acid mixtures
Acetylene	Chlorine, bromine, copper, fluorine, silver, mercury
Alkali and alkaline earth metals	Water, carbon tetrachloride or other chlorinated hydrocarbons, carbon dioxide,
(lithium, sodium, potassium)	halogens, powdered metals (e.g., aluminum or magnesium)
Ammonia(anhydrous)	Mercury (e.g., in manometers), chlorine, calcium hypochlorite, iodine,
	bromine, hydrofluoric acid (anhydrous)
Ammonium nitrate	Acids, powdered metals, flammable liquids, chlorates, nitrates, sulfur, finely
	divided organic or combustible materials
Aniline	Nitric acid, hydrogen peroxide
Arsenical materials	Any reducing agent
Azides	Acids
Bromine	See Chlorine
Calcium oxide	Water
Carbon (activated)	Calcium hypochlorite, all oxidizing agents
Carbon tetrachloride	Sodium, Chlorates, Ammonium salts, acids, powdered metals, sulfur, finely
	divided organic or combustible materials
Chlorine	Ammonia, acetylene, butadiene, butane, methane, propane (or other petroleum
	gases), hydrogen, sodium carbide, benzene, finely divided metals, turpentine
Chlorine dioxide	Ammonia, methane, phosphine, hydrogen sulfide
Chromic acid and chromium	Acetic acid, naphthalene, camphor, glycerol, alcohol, flammable liquids in
	general
Copper	Acetylene, hydrogen peroxide
Cumene hydroperoxide	Acids (organic or inorganic)
Cyanides	Acids
Flammable liquids	Ammonium nitrate, chromatic acid, hydrogen peroxide, nitric acid, sodium
Ĩ	peroxide, halogens
Fluorine	Isolate from everything
Hydrocarbons	Fluorine, chlorine, bromine, chromic acid, sodium peroxide
(e.g., butane, propane, benzene)	
Hydrocyanic acid	Nitric acid, alkali
Hydrofluoric acid (anhydrous)	Ammonia (aqueous or anhydrous)
Hydrogen peroxide	Copper, chromium, iron, most metals or their salts, alcohols, acetone, organic
	materials, aniline, nitromethane, combustible materials
Hydrogen sulfide	Fuming nitric acid, oxidizing gases
Hypochlorites	Acids, activated carbon
Iodine	Acetylene, ammonia (aqueous or anhydrous), hydrogen
Mercury	Acetylene, fulminic acid, ammonia
Nitrates	Sulfuric acid
Nitric acid (concentrated)	Acetic acid, aniline, chromic acid, hydrocyanic acid, hydrogen sulfide,
	flammable liquids, flammable gases, copper, brass, any heavy metals
Nitrites	Potassium or sodium cyanide.
Nitroparaffins	Inorganic bases, amines
Oxalic acid	Silver, mercury
Oxygen	Oils, grease, hydrogen, flammable: liquids, solids, or gases
Perchloric acid	Acetic anhydride, bismuth and its alloys, alcohol, paper, wood, grease. oils
Peroxides, Organic	Acids (organic or mineral), avoid friction, store cold

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Phosphorus (white)	Air, oxygen, alkalis, reducing agents				
Phosphorus pentoxide	Water				
Potassium	Carbon tetrachloride, carbon dioxide, water				
Potassium chlorate	Sulfuric and other acids				
Potassium perchlorate	(see Sulfuric and other acids also chlorates)				
Potassium permanganate	Glycerol, ethylene glycol, benzaldehyde, sulfuric acid				
Selenides	Reducing agents				
Silver	Acetylene, oxalic acid, tartaric acid, ammonium compounds, fulminic acid				
Sodium	Carbon tetrachloride, carbon dioxide, water				
Sodium Chlorate	Acids, ammonium salts, oxidizable materials, sulfur				
Sodium nitrite	Ammonium nitrate and other ammonium salts				
Sodium peroxide	Ethyl or methyl alcohol, glacial acetic acid, acetic anhydride, benzaldehyde,				
	carbon disulfide, glycerin, ethylene glycol, ethyl acetate, methyl acetate,				
	furfural				
Sulfides	Acids				
Sulfuric acid	Potassium chlorate, potassium perchlorate, potassium permanganate (similar				
	compounds of light metals, such as sodium, lithium)				
Tellurides	Reducing agents				
Water	Acetyl chloride, alkaline and alkaline earth metals, their hydrides and oxides,				
	barium peroxide, carbides, chromic acid, phosphorous oxychloride,				
	phosphorous pentachloride, phosphorous pentoxide, sulfuric acid, sulfur				
	trioxide				

Appendix G: CGA numbers for common lab gases and gas mixtures.

If a gas is not listed, you can find the CGA number online and/or from the chemical vendor.

CGA Fittings Required	Pure Gases	CGA Fittings	Mixed Gases	
		Kequired	Minor Component	in Major Component
510/300	Acetylene	240/660/705	Ammonia	Nitrogen
590/546/347/702	Air	350	Butane	Nitrogen
240/660/705	Ammonia	296	Carbon Dioxide	Oxygen
580/680/677	Argon	580	Carbon Dioxide	Helium or Nitrogen
350	Arsine"	580	Carbon Dioxide	Helium
320	Carbon Dioxide	,00	and/or Nitrogen	r icitain
350	Carbon Monoxide	590	Carbon Monoxide	Air
660	Chlorine	330	Chlorine	Nitrogen
510	Cyclopropane	350	Diborane	Areon, Helium,
350	Deuterium			Hydrogen, Nitrogen
350	Ethane	580	Freon-12	Nitrogen
350	Ethylene	296	Helium	Oxygen
510	Ethylene Oxide	350	Hexane	Nitrogen
580/680/677	Helium	350	Isobutane	Nitrogen
/695/703	Hydrogen	590	V	Anna
330	Hydrogen Chloride	280	Krypton	Argon
330	Hydrogen Sulhde	590	Methane	Air
0	Krypton	580	Moisture	Argon, Helium or Nitro
350/695/703	Methane	660	Nitric Oxide	Nitrogen
510	Methyl Chloride	660	Nitrogen Dioxide	Air or Nitrogen
580/680/677	Neon	590	Nitrous Oxide	Nitroren
580/680/677	Nitrogen	500	0	Nimon or Haliam
326	Nitrous Oxide	590	Oxygen	Nitrogen of Helium
540/577/701	Oxygen*	350	Propane	Nitrogen or Helium
350	Phosphine	590	Propane	Air
510	Propane	660	Sulfur Dioxide	Air or Nitrogen
350	Silane*	590	Sulfur Hexaflouride	Argon, Helium or Nitro
668/660	Sultur Dioxide	350	Sulfur Hexaflouride	Hydrogen
590	Sultur Hexaflouride			
580/680/677	Xenon			

Appendix H: Working with Chemicals While Pregnant

The following guidelines are provided for women who work in a laboratory environment and are pregnant, nursing, or are trying to become pregnant. It should be noted that the U.S. Supreme $Court^1$ has determined that a pregnant employee has the right to determine whether or not she continues in her present work environment while pregnant regardless of the hazards that may be present.

1. Creating and following proper laboratory, chemical hygiene, and biological safety procedures is critical in any lab environment. A robust chemical hygiene plan or biosafety plan and standard operating procedures provide the first line of defense for any lab employee.

2. The pregnant employee should start by listing all the hazards to which they might be exposed in the course of their own or a co-worker's work. Don't limit the list to chemical hazards only; many other hazards exist in the lab environment, such as radiation, biological materials, lifting of heavy objects, heat, fatigue, stress, etc.

3. Research the various materials used in the lab. Safety Data Sheets (SDS) are a good place to start your research but do not limit your research to one source. Additional, and often better, information on specific hazards can be found in a chemical dictionary, Prudent Practices in the Laboratory, the Centers for Disease Control website and others.

4. Discuss your list with your doctor or healthcare provider. In some cases it may be prudent to also discuss your concerns with an Occupational Medicine doctor – they have additional expertise in toxicology and other areas directly related to the work environment.

5. Discuss your list of concerns with your supervisor or Principal Investigator.

6. Discuss any recommendations made by your doctor with your supervisor.

7. Although it is not required, it is recommended that the supervisor attempt to accommodate the employee as much as possible. Labs have often made provisions where a person would temporarily have someone else carry out work with a particular agent or chemical. Ultimately it is the responsibility of the employee to determine whether or not they are willing to accept the risks associated with hazards in the laboratory.

8. Consult with Occupational and Environmental Health & Safety (OEHS) at 801-581-6590 to make sure that any steps taken to minimize the hazards are appropriate or if you have any questions.

Section 2. Specialized Safety Information

I. Working with Pyrophorics (Saouma Group)

Standard Operating Procedure

Task: Working with Pyrophoric Chemicals Created by: Saouma Group Date: 05/08/17 Revision Date (Author): 05/15/17 (Saouma)

BACKGROUND:

Failure to follow proper handling techniques can result in serious injury or death.

Pyrophoric chemicals are extremely reactive with air and/or moisture, resulting in spontaneous combustion when exposed to air. This guide serves as an introduction to the hazards and techniques to safely handle pyrophoric materials. It is not a replacement for formal training in lab techniques or lab safety. Only qualified and experienced lab personnel should attempt to manipulate pyrophoric materials, and only after they have completed the appropriate training. Failure to follow proper handling precautions can result in the exposure of these materials to the atmosphere, with consequences including serious injury or death.

Pyrophoric reagents are substances that ignite instantly upon exposure to oxygen, and in most instances, are also water reactive, where heat and hydrogen (flammable gas) are produced. Examples of pyrophoric reagents include:

- Alanes
- Alkyl aluminum reagents
- Alkyl lithium reagents
- Alkyl phosphines
- Alkyl silanes
- Alkyl zinc reagents
- Boranes
- Finely divided metal powders
- Grignard reagents
- Group I/II metals
- Iron pentacarbonyl
- Metal hydrides
- Phosphines
- Sodium/Potassium Alloy (NaK)
- White phosphorus

TRAINING REQUIREMENTS:

Before attempting to use pyrophorics, users MUST consult with the PI and go through the training outlined below. Only after the PI gives permission can the user begin training with a lab safety officer. Only after handling pyrophorics twice under the supervision of a lab safety officer can the user take the written and practical exam to be checked-out to use pyrophorics.

Prior to performing ANY supervised reactions with pyrophorics, users must complete the following:

- ✓ Department of Chemistry Safety Training
- ✓ Saouma Group Safety Training
- ✓ Fully read and understand this SOP
- ✓ Consult with PI

To be fully checked-out, users must additionally complete the following:

- ✓ At least two supervised uses of pyrophorics with a group safety officer (two of which must be done unaided)
- ✓ Pass the written and practical exam administered by the PI
- ✓ OEH&S Fire extinguisher training (part of Chemistry Safety Training) highly recommended

Only upon full completion of these requirements will a user be checked-out for working with pyrophorics. **Note**, the user must still abide by all safety rules, which includes working only when others are around.

POTENTIAL HAZARDS:

Pyrophoric reagents are extremely reactive to oxygen and moisture, and precautions must always be taken to prevent their exposure to air, which usually leads to spontaneous ignition. Matters are often made worse because these reagents are usually sold dissolved in extremely flammable solvents, such as diethyl ether, tetrahydrofuran, or hexanes.

Fires are the primary hazard associated with pyrophoric materials. Fires can result from the chemicals themselves and the solvents containing them, as well as any secondary fires arising after the pyrophorics ignite nearby flammable or combustible materials. Properly storing combustible materials away from work areas is the best way to prevent dangerous secondary fires that could cause serious property damage or personal injury.

SPECIAL PPE AND ENGINEERING CONTROL REQUIREMENTS:

PPE

- Flame-retardant lab coat (blue Nomex)
- Leather gloves on top of clean nitrile gloves
- Safety glasses/goggles (face shield suggested)
- Hair tied back
- Closed-toed shoes and pants
- Clothing with natural fibers (no synthetic fibers due to high flammability)

Safety glasses, gloves, closed-toed shoes, long pants, and a protective flameretardant lab coat must be worn.

Ideally, a blue Nomex lab coat is used, but if none are available, then a 100% cotton coat may be used. *Under no circumstances should a coat that contains synthetic fibers be used.*

Loose clothes and those made of synthetic fibers should be avoided, even under a flame-retardant lab coat. It is thus advised to plan ahead, and to wear appropriate clothes to the lab when working with pyrophorics.

Leather gloves are strongly recommended to be worn above nitrile gloves. These are flame-retardant, minimizing the risk of burns to the hands.

Safety glasses are required, and it is advised that goggles or a blast-shield be used, if available.

Engineering Controls

Due to their extreme reactivity to oxygen and moisture, engineering controls must be followed when working with pyrophorics.

Inert-atmosphere gloveboxes are suitable for the storage of pyrophoric solids and liquids, as well as the manipulation of pyrophorics. **Note**, *pyrophoric solids*, *particularly those that have been purified (e.g., "grey" LAH that has been purified to give the white material), must be stored in an inert-atmosphere glovebox.*

When working with pyrophorics outside of the glovebox, it must be done in an inert atmosphere. Therefore, a *Schlenk manifold* with an inert-atmosphere line must be used to supply an inert atmosphere to chemical reactions, and to provide a pressure difference for cannula transfers/syringe transfers. A mineral oil or mercury *bubbler* must be used to avoid pressure build-up. **Note**, *under no circumstances should you*

use negative pressure (ie vacuum) to manipulate pyrophorics- this increases the risk of inadvertent exposure to air.

If possible, all manipulations should be done in a certified *fume-hood* that is free of clutter and flammables, with the sash lowered to the lowest practical working height. A blast shield is an excellent additional engineering control, if available.

MATERIALS NEEDED:

- Safety sand
- Class D extinguisher (in room)
- Class A/B/C extinguisher (in room)
- Safety shower (in room)
- Blast shield (recommended)
- Toluene/PrOH, iPrOH, and H₂O bottles
- Dry ice in a bucket
- Suitable air- and moisture-free working environment

BEFORE YOU BEGIN:

GENERAL SAFETY

- NEVER work alone.
- NEVER work unless you are 100% focused on the task and 100% comfortable with the procedure, risks, hazards, and are prepared for accidents.
- KNOW all the reactions (main and side) associated with the pyrophoric reagent and all solvents/chemicals being used, as well as with moisture/oxygen.
- ALWAYS fill out an SOC prior to working with pyrophorics.
- ALWAYS secure bottles of pyrophoric reagents in your hood with a clamp.
- ALWAYS use a long needle to avoid tipping bottles of pyrophoric reagents.
- ALWAYS ensure that your work space is free of clutter and flammables.
- ALWAYS ensure that you have safety sand nearby and access to safety showers/extinguishes.
- ALWAYS notify at least one other person in the lab that you are planning to work with pyrophorics, so that you can call on them if you need help.

EMERGENCY PREPAREDNESS AND RESPONSE

When working with pyrophorics, it is imperative that you are prepared for the worst possible scenario. Accidents can and do happen, and being prepared can be the difference between minimal damage/no injury and serious property damage and injury/death. Thus, when going through the training for pyrophorics, it is important that you consider various scenarios, and know how to deal with them if they arise.

You should anticipate fires. Knowing how to deal with them will allow you to think clearly in the moment and avoid panic.

You should always notify others that you plan to work with pyrophorics, so that they are ready to help if needed.

Safety Eyewash and Shower

While safety showers and eyewashes are usually used for chemical contamination on the body, they are also suitable for instances when you may be on fire. **Never** use a fire blanket, as smothering the flames may trap heat and cause deeper burns. The fire blanket may be used to make a shield around the person.

Always know the location of the nearest eyewash and shower, as well as how to use them (see signs near equipment). Before working with pyrophorics, check that both the eyewash station and shower are functional. This usually will involve checking the signage for the last test date. If in doubt, get a bucket and test both. Also be sure that you have a clear path from your work station to the safety shower/eyewash.

Be prepared to remove clothing, especially if you are wearing synthetic fibers which are melting. This likely will involve having lab members of the same gender forming a shield (perhaps with the fire blanket), while those of the opposite go get help. It is a good idea to have a change of clothes with you at lab in the event that you need to change.

Safety Sand and Extinguishers

When working with pyrophorics, it is imperative that you have a bucket (and scoop) of dry safety sand nearby. You should be comfortable lifting and moving it around, and the sand should remain covered when not in use to avoid contamination/moisture. Sand can safely smother flames for all classes of fires, particularly if the fire is small. In addition, it may serve as a place to contain a small fire, for instance, if a kimwipe becomes contaminated with the pyrophoric material. Users of pyrophoric chemicals may also encounter small fires at the tips of needles. Expect this and do not panic.

When working with pyrophorics, you should have an A/B/C dry chemical extinguisher in the room, and you should know how to use it and familiar with its *limitations* (see signage by extinguishers). While the pyrophoric reagent may cause the fire, in most instances, the fire is the result of some nearby fuel (solvent, kimwipe, etc.) catching fire. Thus, in many cases, it is appropriate to use an A/B/C dry chemical extinguisher.

Note, never use a CO₂ extinguisher, as this reacts with pyrophorics in an exothermic reaction and can greatly exacerbate the problem!

When working with neat pyrophoric materials (such as K metal, fine powders, or LAH solid), you should have a D extinguisher in the room and know how to use it and familiar with its limitations (see signage by extinguishers). For these fires, an A/B/C

extinguisher is NOT appropriate. As a first measure, sand may be used to smother these fires.

Quenching

The user of pyrophorics should be aware of the reactivity of the pyrophoric material, and therefore how to quench it. In most instances, quenching is done by first adding a solution of toluene/isopropanol, followed by isopropanol, followed by water. However, in some instances, this will not be sufficient. For example, phosphines must be quenched with bleach. As phosphines may be prepared with Grignards or other pyrophoric nucleophiles, it is imperative to quench with alcohols/water then with bleach. Generic details are given later in this SOP. For reagants that require additional quenching considerations, consult the appropriate SOP or Prudent Practices.

STORAGE

When storing pyrophoric reagents for long periods of time after the initial use, the integrity of the reagent may be compromised. Thus, it is highly recommended that pyrophoric reagents are purchased in quantities that will be used in each experiment to avoid the storage of excessive amounts of these hazardous chemicals. If storage is required, make sure that the head space is always purged with an inert gas prior to storage.

Pyrophorics should always be stored under an inert atmosphere. While storage in an inert-atmosphere glovebox is ideal, it is not always practical. Though less ideal, they may also be stored in a desiccator that is sealed and flushed with an inert atmosphere. Unopened containers may be segregated from other chemicals and stored in flammable cabinets. *Opened containers of pyrophorics MUST be stored in a dedicated, explosion and flame-proof fridge.* This is because they are incompatible with all other chemicals and the risks are much greater once a container has been opened.

Solids

Solids are generally more stable to air than solutions/liquids, but caution must also be exercised when storing them. They should always be stored in an inert environment.

Some solids such as Li, Na are sold as dispersions or blocks under mineral oil, to reduce oxidation on the surface. Removal of the mineral oil is accompanied by cutting a piece of the alkali metal (under oil) and transferring it to a flask containing a hydrocarbon such as heptane to rinse off the oil.

Note, *K* is sold under mineral oil, but it MUST be stored either in a glovebox or destroyed after ~ 3 months. Potassium oxidizes to give potassium superoxide, which

is a yellow, shock-sensitive peroxide that can explode upon handling. This will usually form along the rim of the container, so an explosion can ensue upon opening.

Note, *Li* must be stored under Ar, as it reacts with N_2 to form lithium nitrides, which is explosive. It is therefore best to keep Li in oil, in a sealed container that is purged with Ar.

Mildly pyrophoric reagents such as LiAlH₄ (the grey, impure stuff) are typically sold as solids in a bag in a bag in a sealable metal can. Care must be taken to avoid contaminating the rim with the pyrophoric solid, as this will impact the seal and may increase the likelihood of an accident. These materials can be handled in air for short periods of time. **Note**, as a solution or in pure form, LiAlH₄ becomes extremely pyrophoric.

Liquids

Liquid pyrophorics, or solutions of pyrophorics in solvent, are generally less stable to air than solids. There is the added hazard that the solvent serves as a fuel, making fires more likely and dangerous.

Storing solutions of pyrophoric reagents for a long time may affect the integrity of the solution; the reagent may become more concentrated due to solvent evaporation (particularly if stored in a glovebox), or less concentrated due to reaction with trace oxygen/moisture (particularly if stored outside of a glovebox). It thus is recommended that the user of pyrophorics titrate their solution, to ensure proper stoichiometry.

Most liquid pyrophorics are sold in a sealed bottle with a Sure/Seal cap (or equivalent). Over time, the integrity of the Sure/Seal may be compromised, allowing trace oxygen/moisture in. To avoid this, users have four options:

- 1. Store the reagent in an inert atmosphere glovebox. Be sure to only bring in new bottles with a Sure/Seal, have the bottle upright in the anti-chamber, and mark the level of liquid before/after bringing it in. This is to ensure that the seal was not compromised.
- 2. Transfer the reagent to a Strauss flask or Schlenk tube with a Teflon plug that separates the reagent from a ground-glass joint. When using the reagent, the user then flushes the side-arm with inert gas, opens the plug, and quickly replaces the plug with a suitable septum which is tightened.
- 3. Attach a special re-sealable cap from Aldrich (product no: Z406260-1EA or Z407186-1EA).
- 4. Cap the bottle and electrical tape it shut. This offers the least amount of protection.

Liquid pyrophorics should be stored at reduced temperatures to minimize the risk of reactions with moisture/oxygen. Prior to using the reagent, it should be warmed to room temperature to ensure that the reagent is fully dissolved, the density is as predicted, and to minimize trace moisture contaminating the reagent when puncturing the bottle with needles.

EQUIPMENT PREPARATION

The following assumes the use of a Sure/Seal or similar PTFE-sealed glass bottle. Similar procedures could be used for any flask that is affixed with a rubber septum. Either a syringe or a double-tipped needle (cannula) can be used for the reagent transfer.

Needles

Longer needles are better, so that the syringe can easily reach the liquid in the bottle. Needles with a locking mechanism (e.g. Luer-Lock) are highly recommended to ensure that the needle does not disconnect from the syringe, causing a spill and fire. If a disposable syringe is being employed with a Luer-Lock, it is best to tighten the needle gently with a wrench- overtightening will strip the locking mechanism giving rise to leaks, and improper tightening will also result in leaks.

Sixteen-gauge needles are recommended for most applications. Smaller gauge needles are prone to clogging, either at the tip when transferring to your reaction, or internally due to precipitate in the pyrophoric solution. Larger gauge needles are also not recommended, as the puncture hole will leave too large a hole for the septum to re-seal, causing leaks. This mainly applies to repeated Sure/Seal applications. **Note**, if the pyrophoric reagent is stored in a flask that is capped with a Teflon plug, and thus with each use a fresh septum is used, this is not a concern.

Both stainless steel and Teflon needles can be used. Stainless steel is advantageous as they are easier to work with, but Teflon are convenient because they do not need to be dried, and clogs are visible. To use a Teflon needle, be sure to cut the tip at an angle, and push the needle though a septum (not Suba-Seal) that has previously been pierced with a needle one size larger than that of the Teflon needle).

The same considerations must be taken into account when using a cannula (double-tipped needle).

Syringes

Regardless of the syringe type, a locking mechanism must be present to attach to the needle. The total syringe volume must be at least 2x that of the liquid being transferred (ideally 3x).

Ideally, a gas-tight syringe will be used. As these are glass, it is important that they are washed, dried, and stored in a desiccator until being used. As an extra pre-caution, it is advised that the syringe is rinsed 1-2 x with dry solvent (same solvent as your reaction), to rinse away any trace moisture. If a gas-tight syringe is not available, then a disposable syringe may be used.

Syringes can only be used for transferring < 10 mL or reagent. They should NEVER be used to transfer ^tBuLi.

Schlenk Line

An inert gas line for supplying positive nitrogen pressure to the reagent bottle and reaction flasks must be prepared. Dry, high quality nitrogen or argon (no more than 5 psi) should be affixed to a manifold that is equipped with a mercury or mineral **oil bubbler**. Thick rubber tubing delivers the inert gas from the manifold to the reaction flask and reagent bottle, either by direct attachment of the rubber hosing, or via a Luer-Lock adaptor that connects the hose to a needle.

Glass wear

Only use glassware that has been oven-dried for at least 4 hours (to remove all moisture), and cooled under vacuum or under an inert atmosphere.

Work Space

The work space must be free of clutter, and in particular, free of any potentially flammable materials. Clamps must be in place to clamp all flasks and reagent bottles. In addition, safety sand must be nearby. It is recommended that extra septa, copper wire, and pliers be present, in case a bottle or flask must quickly be sealed.

PROCEDURE: Transferring Liquid Pyrophoric Reagents Outside the Inert Atmosphere of a Glovebox

PROCEDURE: SYRINGE TRANSFER

1. Prepare your Shlenk line.

- **1.1.** Turn on the nitrogen, and flush the manifold for at least 5 minutes.
- **1.2.** Check to ensure that all taps are closed, except those that will be used.
- **1.3.** Check to ensure flow to the taps that you will be using. Be sure to check this after needles have been attached, as needles can become clogged.



2. Prepare your work space.

2.1. Remove all flammables.

2.2. Organize your work space so that the reagent bottle is closest to the nitrogen inlet and your reaction is further away from it (taps from the manifold). Both should be between the nitrogen inlet and the bubbler.

2.3. Clamp your reaction flask and reagent bottle.

- 2.4. Attach all flasks (reaction and reagent bottle) to your inert gas line.
- **2.5.** If you are cooling your reaction flask, cool the flask and ensure that there is appropriate stirring.



3. Flush your syringe-needle assembly.

- **3.1.** After you have attached your needle to your syringe, fill the syringe with air, insert the needle into a rubber stopper and compress the syringe. The plunger should depress to ~ half its original volume if there are no leaks. If it can be further compressed, check for leaks.
- **3.2.** With the syringe empty, pierce the septum on your reaction flask, withdraw a syringe full of inert atmosphere, remove the assembly from the septum, and push out the inert atmosphere. Repeat this 3x, then "store" your syringe/needle assembly under the inert atmosphere of your reaction flask.

4. Fill your syringe with your reagent.

4.1. Fill the syringe one final time with inert atmosphere, remove from your reaction flask, and push out the inert atmosphere right before you pierce the Sure/Seal of your reagent flask with the needle.



4.2. With the needle below the reagent line, slowly pull the plunger back to fill the syringe with the required volume.

4.2.1. **Note:** Never tip the reagent bottle. Tipping increases the chance of leakage, which can then catch fire.

4.2.2. **Note:** If air/gas is filling your syringe, immediately stop. This indicates that there may be a leak. Notify others, then carefully remove the needle from the Sure/Seal, and place the entire syringe/needle assembly in a bucket of dry ice. Very carefully push out the reagent, which will be guenched with the dry ice. Be prepared with sand in

case a fire ensues. Alternatively, transfer the entire assembly to a flask that is under N_2 , and under a strong counter flow, carefully push out the solution. Quench as usual.

4.3. Once the required volume is attained, slowly pull the needle from the pyrophoric reagent to the overhead space above the liquid.



4.4. Slowly pull the plunger up to allow the inert gas to push the reagent trapped in the needle into the syringe. This creates a buffer of inert gas between the reagent and the tip of the needle. **Note**, take into account this extra volume.

5. Transfer the pyrophoric liquid.

5.1. Carefully remove the needle from the reagent bottle. It is advised that you keep the syringe inverted, such that the buffer of inert atmosphere is maintained between the

solution in the syringe and the tip of the needle.

5.2. Working quickly, puncture the septum on your reaction flask with your needle, and push the plunger of your syringe in at the appropriate rate.

6. Cleaning up.

- **6.1.** Once the transfer is complete, the inert gas supply to the reagent bottle is shut off.
- **6.2.** The syringe/needle is removed from the reaction flask. **Note**, if a flame is present, then it is extinguished in sand.
- **6.3.** The needle/syringe must immediately be cleaned to avoid clogging the bore, and potentially trapping reactive materials inside. This is done by drawing toluene into the syringe and flushing the contents into an Erlenmeyer flask. This is repeated for a total of 3x, at which time the needle and syringe can be separated. The syringe should be rinsed with a solution of isopropanol in toluene, then isopropanol, then water, to ensure complete quenching. The syringe may then be disposed of. The needle is then rinsed with the same sequence of solvents, and finally acetone (to avoid rust forming on the inside). Note, you must ensure that any trace pyrophoric compounds in your solvent

wash has been quenched. Upon addition of isopropanol, look for bubbles and/or warming of the flask. If the mixture is exotherming, cool the flask in dry ice. Once quenched, the mixture can be added to the appropriate waste stream.

6.4. Return the pyrophoric reagent to its storage area.

PROCEDURE: CANNULA TRANSFER

N2 in

The overall process is similar to that described above.

Prepare your Shlenk line.

- **6.5.** Turn on the nitrogen, and flush the manifold for at least 5 minutes.
- **6.6.** Check to ensure that all taps are closed, except those that will be used.
- **6.7.** Check to ensure flow to the taps that you will be using. Be sure to check this after needles have been attached, as a common place for clogs is in the needles.

7. Prepare your work space.

7.1. Remove all flammables.



bubbler

Schlenk line

- **7.2.** Organize your work space so that the reagent bottle is closest to the nitrogen inlet, your graduated cylinder (if using) is in the middle, and your reaction is furthest away from it (taps from the manifold). All should be between the nitrogen inlet and the bubbler.
- **7.3.** Clamp all of your flasks and reagent bottle, as well as any flasks that you may be using to measure out your reagent (e.g., a graduated cylinder). **Note**, you may want to clamp your reagent bottle on an elevated surface, to facilitate the cannula transfer.
- **7.4.** Attach all flasks (reaction, graduated cylinder if using, and reagent bottle) to your inert gas line.
- **7.5.** If you are cooling your reaction flask, cool the flask and ensure that there is appropriate stirring.

8. Connect the reagent bottle to your receiving flask.

- **8.1.**Carefully pierce the Sure/Seal of the reagent flask with one end of your cannula. Be sure to keep the needle well above the liquid line.
- **8.2.** Ensure that there is flow through the needle.
- 8.3. Pierce the other end of the cannula to your receiving flask.

9. Transfer your reagent.

9.1. Add a vent needle to your receiving flask.

- **9.2.** Carefully lower the cannula into the pyrophoric reagent. While you do this, watch the receiving flask for transfer of the liquid. There may be some, which is okay.
- **9.3.** Close the inert gas tap to your receiving flask (slowly), to facilitate the transfer. **Note**, you may need to lower your receiving flask, and/or slowly and gently raise the pressure of your reagent flask.
- **9.4.** Allow the solution to transfer. **Note**, the flow rate can be controlled by changing the pressure difference. This is readily done by using a smaller gauge needle as a vent, and/or having a slight inlet of inert gas into the receiving flask.
- **9.5.** When complete, raise the cannula out of the reagent flask and allow the liquid in the needle to fully transfer.
- 9.6. Open your receiving flask to inert atmosphere.
- **9.7.** Remove your vent needle.
- **9.8.** If you were transferring the liquid directly to your reaction, then you are done and can proceed to step 6. If you transferred your solution to a graduated cylinder, then proceed to step 5.

10. Complete the second cannula transfer.

- **10.1.** With all flasks under inert atmosphere, and the cannula empty of solution (both ends above the solvent line), pull the cannula out of the reagent flask and quickly transfer the tip to your reaction flask. If a flame is present, quickly extinguish with sand.
- **10.2.** Repeat step 4 to complete your transfer.

11. Cleaning up.

- **11.1.** Once the transfer is complete, the inert gas supply to the reagent bottle is shut off.
- **11.2.** The cannula is removed, and rinsed with toluene, then a solution of isopropanol in toluene, then isopropanol, then water, to ensure complete quenching. Finally, it is rinsed with acetone. This washing step is readily done by placing a receiving flask under partial vacuum (house vacuum) and attaching one end of the cannula to this flask and the other to a flask that contains the various solvents. **Note**, monitor the solvent wash for bubbles and/or warming of the flask. If the mixture is exotherming, cool the flask in dry ice. Once quenched, the mixture can be added to the appropriate waste stream.
- **11.3.** The graduated cylinder (if used) is washed. The inert gas supply is removed, as is the septum. The cylinder is rinsed with 3x toluene, then a solution of isopropanol in toluene, then isopropanol, then water, to ensure complete quenching. **Note**, monitor the solvent wash for bubbling or an exothermic reaction. Upon addition of isopropanol, look for bubbles and/or warming of the flask. If the mixture is exotherming, cool the flask in dry ice. Once quenched, the mixture can be added to the appropriate waste stream.
- **11.4.** Return the pyrophoric reagent to its storage area.

PROCEDURE: Transferring Pyrophoric Reagents Inside an Inert Atmosphere Glovebox

Pyrophoric reagents can be conveniently and safely handled in a glovebox. Often, the SureSeal is removed to facilitate the transfer of the liquid reagent. If the Sure/Seal has not been removed, then it is imperative to inject an equal volume of glovebox atmosphere into the reagent bottle as is being withdrawn, to maintain the pressure inside and facilitate reagent withdrawal via syringe. It is also important to bring in a long needle to again avoid tipping the reagent bottle – after an initial puncture, the Sure/Seal will be prone to leaking.

It is also imperative that the user brings in an extra pair of nitrile gloves, to wear on top of the butyl gloves, when working with pyrophorics. This serves two purposes. First, it avoids accidental contamination of the gloves, which can then transfer pyrophoric material to other things in the glovebox, and can lead to an unexpected fire when taking things out of the glovebox. Second, it protects the gloves. Certain pyrophoric reagents such as BuLi degrade the gloves.

Finally, the user must be very aware of everything that touches the pyrophoric material, and care must be taken to quench these items/carefully remove them from the glovebox (see later).

Preparing reagents in the glovebox

A safe and convenient alternative to the Schlenk techniques described above is to load a syringe inside the glovebox. In this approach, the reagent is already stored in the glovebox. It is best practice to remove the SureSeal cap with a vial, to facilitate removal of the solution without inverting. Also, nitrile gloves should be work above the glovebox gloves, to minimize degradation of butyl gloves/contamination. After loading a syringe (< half full, and with a blanket of inert atmosphere), the needle is capped by placing the tip in a rubber septum, avoiding contamination with air upon removal from the glovebox. Using appropriate PPE, the needle/syringe is then taken from the antechamber to the Schlenk line, where the reagent is added as describe above by piercing the needle through the septum.

Alternatively, the reagent can be loaded into a Schlenk flask, which is capped and removed from the glovebox. Subsequently, cannula transfer into your reaction flask, as described above, is done. This is a convenient method for preparing solutions of pyrophorics that are sold/stored as solids. This technique is preferred over the syringe method, as it removes the potential hazard of a Luer-Lock failure, and allows the pyrophoric reagent to be stored under an inert atmosphere during a slow addition to your reaction.

Using reagents in the glovebox

Both liquid and pyrophoric reagents can readily be used inside the glovebox. The user should ensure that the proper temperature can be attained inside the glovebox.

Removing waste from the glovebox

Perhaps the greatest source of fires when working with pyrophorics comes from the removal of waste from the glovebox antechamber. It is imperative that the user be cognoscente of what the pyrophoric material came into contact with, and that items such as spatulas be wiped down, and the kimwipe/contaminated materials be kept segregated from the common glovebox trash. Users should only remove contaminated material during the day, when others are around, and when they are 100% committed to the task. If this waste is stored short term in the glovebox, it should be labelled as such so that it is not accidently removed. "Fire" or "pyrophoric" are suitable labels.

In removing the items, the user must always wear appropriate PPE, have a clear path from the antechamber to their hood, a clean hood, and be equipped with sand, dry ice, and squirt bottles of toluene, toluene/isopropanol, isopropanol, and water.

Ideally, reagents are quenched inside the glovebox. Some pyrophorics, such as BuLi, react with ethers at room temperature. Thus, in many reactions run in ethereal solvents, any pyrophoric material left over has been quenched. This is not the case with Grignards, however, and other pyrophoric materials.

Waste solutions can readily be quenched by adding MeOH dropwise (or MeOH in toluene) to the pyrophoric solution until no bubbling/exothermic reaction occurs (be sure to turn the circulator off and purge the glovebox!). **Note**, it may be advised to calculate the volume required to quench all of the pyrophoric material assuming no reaction has occurred. The solution is then capped and loaded to the antechamber. The flask is then immediately placed in dry ice, and taken to a hood where the cap is removed. More alcohol then water is added, to ensure full quenching, prior to waste disposal.

In a similar manner, kimwipes, frits, etc. can be quenched by rinsing them in the glovebox first with toluene, then with MeOH in toluene. The waste solvent is taken out as described above. While the kimwipes, frits, etc. should be quenched, they should be taken out cautiously and one at a time. Kimwipes can be placed in capped vials, which are removed to a dry ice (or sand) bucket, and carefully opened/quenched again. Frits are removed in a similar manner. If a pyrophoric solid must be quenched, it is done so by preparing a suspension (using an inert solvent) in the glovebox and quenching as described above.

If quenching inside the glovebox is not an option, then extreme caution must be taken. You should assume that a fire will ensue. All quenching should be done in your hood, and transfer from the box to your hood be done either in a sand bucket or a bucket filled with dry ice. **Note**, you should never add fuel to a fire, so if a fire is burning, do not try to "quench" it. Rather, smother it with sand or the appropriate extinguisher.

For solutions/liquid pyrophoric waste, the flask is sealed, removed, cooled with dry ice, and quenched as described above. If appropriate, you may want to attach the flask to your Schlenk line and quench under an inert atmosphere.

Na/Hg can be removed as is, and toluene/isopropanol added above the amalgam and stirred in the hood.

Frits, including those that have celite which may contain a pyrophoric material, should carefully be loaded to the antechamber (perhaps capping with a septum), then quickly inverted to a sand bucket and take to a hood. If a fire ensues, smother it with sand (using a spatula as a rake is a good idea). Carefully rake the sand to ensure no more sparks/fire, and that the pyrophoric has completely quenched. You may want to then moisten the sane with toluene/isopropanol then isopropanol then water to ensure complete quenching.

Kimwipes are removed in a similar manner. The kimwipe should be placed in a vial, which if capped, is placed in a dry ice bucket upon removal from the glovebox. It is then carefully opened (once cold), and quenched as described above. If the vial is not capped, then it is quickly inverted over sand, as described for frits.

All glassware should be removed and placed either in a sand or dry ice bucket, taken to a hood, and rinsed with the quenching solvents.

PROCEDURE: Transferring Solid Pyrophoric Reagents Outside the Inert Atmosphere of a Glovebox

Solid pyrophorics should only be handled inside a glovebox. In some instances, a mildly pyrophoric reagent such as LAH (grey, tech grade), may be handled under air for short periods of time. In all instances, it is recommended that the solid reagent be loaded to a flask, and under an inert atmosphere, solvent be transferred to it. The solution is then cannula transferred into your reaction. If this is not possible, then the solid may be added via a solid addition funnel. **Note**, care must be taken to avoid contamination of the joints with the pyrophoric material, as friction from removing the joint may be sufficient to start a fire. Thus, disassembly of the reaction flask must be done carefully.

REFERENCES AND RELATED SOPS:

- PNNL's Guide for Handling Pyrophoric Reagents: <u>https://www.pnl.gov/main/publications/external/technical_reports/PNNL-18668.pdf</u>
- Alex Miller (UNC) SOP
- Aldrich Technical Bulletin AL-164: <u>http://www.sigmaaldrich.com/content/dam/sigma-</u> <u>aldrich/docs/Aldrich/Bulletin/al_techbull_al164.pdf</u>
- Alnajjar, M.; Quigley, D.; Kuntamukkula, M.; Simmons, F.; Freshwater, D.; Bigger, S., *Journal of Chemical Health and Safety* **2011**, *18*, 5-10.
- Schwindeman, J. A.; Woltermann, C. J.; Letchford, R. J., *Chemical Health and Safety* **2002**, *9*, 6-11.
- Rainer, D., Journal of Chemical Health and Safety 2009, 16, 45-46.

• **Prudent Practices in the Laboratory:** https://www.nap.edu/catalog/12654/prudent-practices-in-the-laboratory-handlingand-management-of-chemical

Written and Practical Exam

You must complete the written portion of the exam before moving on to the practical exam.

Written Exam

1. What type of clothing and PPE do you need to work with pyrophorics?

2. When can sand be used to put out a fire?

3. When can a class A/B/C extinguisher be used?

4. When should you use a type D extinguisher?

5. What information do you need to put on your SOC prior to working with pyrophorics in your hood?

- 6. Where are pyrophorics stored in the Saouma labs?
- 7. You are planning to syringe transfer a pyrophoric reagent in your hood. You fill your syringe with air, stick the tip in a septum, and compress the air. You can easily fully suppress the plunger. What does this mean, and what must you check for/now do?

8. You are pulling up your pyrophoric reagent into a syringe, when you notice many bubbles forming in the syringe. What is happening, and what should you do?

- 9. You are syringe transferring a pyrophoric. You fill your syring with pyrophoric solution and a nitrogen blanket. When you pull the needle out of the reagent bottle, some pyrophoric material splashes out.
 - a. What should you do, assuming the drops resulted in no fire?

b. And if the drops did catch fire?
10. While syringe transferring your pyrophoric reagent into your reaction flask, you notice that there is a leak at the LuerLock. What do you do?

11. You just finished cannula transferring a pyrophoric reagent into your reaction, and your Sure Seal bottle is now empty. How do you quench it?

12. Is it okay to unclamp your reagent bottle to invert it to facilitate syring transfers? Explain.

13. Explain how you would cannula transfer a pyrophoric reagent that is stored in a Strauss flask into a graduated cylinder (just the steps to get the needle into the solution).

- 14. You just worked with BuLi in the box. How do you take out your pipette tip that touched the BuLi?
- 15. Likewise, you are now done with your reaction that used BuLi in the box. You are isolating a solid that precipitates out of solution so you filtered the solid, collected it on a frit, washed it with pentanes, and put it in a vial.
 - a. How do you take the filterate out of the box?

b. In drying the solid on the vac line, you accidently got some on the kimwipe in the septum. How do you dispose of this kimwipe?

16. You are loading a RB with a pyrophoric reagent in the box. You put it in the AC, accidently pull vacuum, and you hear the spetum pop. What do you do?

17. You have a kimwipe soaked in BuLi and some pentanes in a vial that is capped. You opt to not quench in the box. How do you take it out/take care of it?

18. When can you work with pyrophorics alone?

Name:_____

Date:_____

Saouma Signature:_____

User Signature:_____

(Written) Score and Comments:_____

Practical Exam

Date/initials of student and PI next to each task once complete. Space is provided to give details of the training.

1. Quenching.

a. The user has quenched a flask with trace pyrophoric reagent.

b. The user has taken out a pyrophoric solid from the glovebox and quenched it safely.

c. The user has taken out a pyrophoric solution from the glovebox and quenched it safely.

2. Syringe transfers. The user has safely syringe transferred a pyrophoric. This includes quenching.

3. Cannula transfers. The user has safely cannula transferred a pyrophoric. This includes quenching.

Name:_____

Date:_____ Saouma Signature:_____

User Signature:_____

(Practical) Score and Comments:

II. Working with Lasers (Morse Group)

Introduction

The purpose of this document is to inform personnel who will be using Class 3b or 4 lasers within this laboratory of the hazards and necessary safety procedures surrounding the use of such equipment. It is extremely important to be safe when operating or present near lasers, especially those classified as Class 3b or 4, as they can produce injuries (including burns, blindness, and electrocution) if improperly used.

What is a laser?

LASER is an acronym that stands for Light Amplification by Stimulated Emission of Radiation. The radiation emitted by the laser is in or near the optical portion of the electromagnetic spectrum, and is emitted in a collimated beam. Energy is amplified to extremely high intensity by a process called stimulated emission. The term "radiation" is often misinterpreted because this term is also used to describe the ionizing radiation that is emitted by radioactive materials. The electromagnetic radiation emitted by lasers is quite different from that emitted by radioactive materials, and is generally not considered to be ionizing radiation. As a result, the hazards associated with laser radiation are completely different than those associated with radioactive materials. As used in the context of a laser, radiation refers to the transfer of energy in the electromagnetic field. Energy moves from one location to another by conduction, convection, and radiation. In a laser, the energy transfer only occurs through radiation. The color of laser light is normally expressed in terms of the laser's wavelength. The most common unit used in expressing a laser's wavelength is the nanometer (nm). There are one billion nanometers in one meter (1 nm = 1×10^{-9} m). Laser light is nonionizing and includes ultra-violet (100-400 nm), visible (400-700 nm), and infrared (700 nm-1 mm).

Electromagnetic Spectrum

The electromagnetic spectrum is vast, ranging from the short wavelength gamma rays to the long wavelength radio waves. Most importantly, the visible portion of this spectrum is very small. The vast majority of the electromagnetic spectrum is invisible to the human eye, which can lead to safety concerns, depending on the type of radiation.

Classification of Lasers

Lasers are divided into a number of classes depending upon the power or energy of the beam and the wavelength of the emitted radiation. Laser classification is based on the laser's potential for causing immediate injury to the eye or skin and/or potential for causing fires from direct exposure to the beam or from reflections from diffuse reflective surfaces. Since August 1, 1976, commercially produced lasers have been classified and identified by labels affixed to the laser. In cases where the laser has been fabricated in house or is otherwise not labeled, Radiation

Safety should be consulted on the appropriate laser classification and labeling. Lasers are classified using physical parameters of the laser, power, wavelength, and exposure duration.

• Class 1 Lasers

- Class 1 lasers are considered to be incapable of producing damaging radiation levels, and are therefore exempt from most control measures or other forms of surveillance.
- Example: Laser printers and CD players.

• Class 2 Lasers

- Class 2 lasers emit radiation in the visible portion of the spectrum, and protection is normally afforded by normal human aversion response (blink reflex) to bright radiant sources. In general, the human eye will blink within 0.25 seconds when exposed to Class 2 laser light. This blink reflex provides adequate protection. However Class 2 lasers emit laser light in the visible range and are capable of creating eye damage through chronic exposure.
- Examples: Laser pointers, surveying lasers.
- Class 2a lasers are special-purpose lasers not intended for viewing. Their power output is less than 1 mW. This class of lasers causes injury only when viewed directly for more than 1,000 seconds. The 1,000 seconds is spread over an 8-hour day, not continuous exposure.
- Example: Many bar-code readers fall into this category.

• Class 3 Lasers

- Class 3a lasers are those that normally would not produce injury if viewed only momentarily with the unaided eye. They may present a hazard if viewed using collecting optics, e.g., telescopes, microscopes, or binoculars.
- Example: HeNe laser above 1 mW but not exceeding 5 mW radiant power, or some pocket laser pointers.
- Class 3b laser light will cause injury upon direct viewing of the beam and specular reflections.
- Example: Visible HeNe laser above 5 mW but not exceeding 500 mW radiant power.

• Class 4 Lasers

- Class 4 lasers include all lasers with power levels greater than 500 mW radiant power. They pose eye hazards, skin hazards, and fire hazards. Viewing of the beam and of specular reflections or exposure to diffuse reflections can cause eye and skin injuries. All of the control measures explained in this training must be implemented.
- Example: Most Nd:YAG Lasers, Excimer Lasers, pulsed dye lasers.

Laser Beam Hazards

The laser produces an intense, highly directional beam of light. If directed, reflected, or focused upon an object, laser light will be partially absorbed, raising the temperature of the surface and/or the interior of the object, potentially causing an alteration or deformation of the material. These properties, which have been applied to laser surgery and materials processing, can also cause tissue damage.

In addition to these obvious thermal effects upon tissue, there can also be photochemical effects when the wavelength of the laser radiation is sufficiently short, i.e., in the ultraviolet or blue region of the spectrum. Today, most high-power lasers are designed to minimize access to laser radiation during normal operation. Lower-power lasers may emit levels of laser light that are not a hazard.

The human body is vulnerable to the output of certain lasers, and under certain circumstances, exposure can result in damage to the eye and skin. Research relating to injury thresholds of the eye and skin has been performed in order to understand the biological hazards of laser radiation. It is now universally accepted that the human eye is more vulnerable to injury than human skin. It is useful to understand the damage that can occur to the human eye as a result of laser exposure, which depends significantly on the wavelength.

190-315 nm:

The cornea (the clear, outer front surface of the eye's optics), unlike the skin, does not have an external layer of dead cells to protect it from the environment. In the deep ultraviolet regions of the optical spectrum (190-315 nm), the cornea absorbs the laser energy and may be damaged. Indeed, radiation of these wavelengths is used for laser radial keratotomy, which is the reshaping of the cornea to improve vision by correcting the refraction of the eye, so that images are focused on the retina. At much lower exposures than is used in radial keratotomy, the cornea can become inflamed (keratitis), leading a delayed sensation of sand in the eyes 6-12 hours after exposure. This condition is typically treated by rest and usually heals after 24-48 hours. Exposure of the skin

to wavelengths of 190-315 nm leads to a "sunburn", which is not typically any more serious than a sunburn caused by exposure to sunlight.

315-400 nm (UV A radiation):

In the 315-400 nm range, the lens of the eye may be vulnerable to injury. Exposure to these wavelengths may increase the risk of cataract formation in the lens of the eye.

400-1400 nm:

Of greatest concern is laser exposure in the retinal hazard region of the optical spectrum, approximately 400 nm (violet light) to 1400 nm (near-infrared) and including the entire visible portion of the optical spectrum. Within this spectral region collimated laser rays are brought to focus on a tiny spot on the retina. In order for the worst case exposure to occur, an individual's eye must be focused at a distance and a direct beam or specular (mirror-like) reflection must enter the eye. The light entering the eye from a collimated beam in the retinal hazard region is concentrated by a factor of 100,000 times when it strikes the retina.

Therefore, a visible, 10 mW/cm² laser beam would result in a 1000 W/cm² exposure to the retina, which is more than enough power density (irradiance) to cause damage. If the eye is not focused at a distance or if the beam is reflected from a diffuse surface (not mirror-like), much higher levels of laser radiation would be necessary to cause injury. Since this ocular focusing effect does not apply to the skin, the skin is far less vulnerable to injury from these wavelengths.

Within this wavelength range, pulsed lasers present serious hazards to the eye. In the Morse group, we work with lasers having a 5 ns pulse duration, which is far shorter than the blink reflex (about 0.25 s). Thus, the entire pulse is focused onto the retina before the blink reflex kicks in. Further, the focusing effect magnifies the danger, so that even weak partial reflections from a flat surface (such as a prism or clear window) become quite hazardous. In addition to burns to the retina, shock and acoustic waves caused by the focused radiation can also cause damage, including retinal detachment. For this reason, it is essential that all reflections or partial reflections should be blocked in the lab, and that laser beam blocks should always be left in place. Reflected beams having energies as low as $25 \,\mu$ J have been known to cause permanent eye damage, so extreme care is required in blocking all specular reflections from surfaces such as prisms, optical filters, lenses, and windows.

<u>Non-Beam Hazards</u>

In addition to the direct hazards to the eye and skin from the laser beam itself, it is also important to address other hazards associated with the use of lasers. These non-beam hazards, in some cases, can be life-threatening, e.g. electrocution, fire, and asphyxiation. The only fatalities from lasers have been caused by non-beam hazards.

• Chemical Hazards:

- Compressed Gases careful handling of compressed gas tanks is important. Reinforce all tanks by attaching them to sturdy objects, e.g. walls or other fixed objects. Poisonous gases must be housed within a well-ventilated cabinet whose exhaust is piped into the fume hood exhaust.
- Laser Dyes and Solvents Many dyes, and some solvents, used in this lab are toxic, carcinogenic, or mutagenic. Even if it is not known whether a dye or solvent falls within one of these categories, it should always be assumed that it does. Take care when handling these substances, wearing gloves and safety glasses to prevent splashes to the eyes. Take extra caution when using dimethylsulfoxide (DMSO) as a solvent. This solvent is known to carry dissolved substances (such as laser dyes) through the skin and into the bloodstream. Make sure to dispose of any used dyes and solvents appropriately by collecting them in labeled containers and arranging for EHS (Environmental Health & Safety) to pick them up.

• Electrical Hazards

- Shock and electrocution are the primary lethal hazards associated with lasers and laser systems, especially their high voltage power supplies. In order to avoid electrical hazards, care should be taken during servicing, testing, modification, maintenance, or any other activity that requires contact with energized components of the laser system. Electrical protection parameters, connection to the utilization system, and safety training should comply with OSHA, the National Electric Code (NEC), National Fire Protection Association (NFPA), and any other applicable state and local laws and regulations.
- Class 3b and 4 lasers should have a separate circuit and local disconnect switch for the circuit.
- It is good practice to have at least two persons in an area while working on highenergy power systems.
- Keep cooling water connections away from main power and high voltage outlets and contacts. Use double hose clamps on cooling water hoses. Inspect cooling water hoses and connections, and power cables and connectors periodically as part of a regular equipment inspection.
- In labs where laser power supplies are opened or serviced by lab personnel, staff should be trained in cardiopulmonary resuscitation.

• Fire Hazards

 Fires can result from contact of a laser beam with flammable materials, unprotected wire insulation, and plastic tubing. While class 4 laser beams present the highest hazard potential for fire (irradiance exceeding 10 W/cm⁻² or beam power above 0.5 W) class 3b lasers may pose a hazard under some conditions. Each of the laser laboratories in the Morse group is equipped with an emergency power shutoff switch and a fire extinguisher. Personnel working in the labs should know the location of these items and how to use them in the event of an emergency.

Eve Protection

Laser protective eyewear is specific to the types of laser radiation in the lab. Each laser laboratory must provide laser-specific appropriate eye protection for persons working with the laser. Windows where Class 2, 3, or 4 beams could be transmitted causing hazards in uncontrolled areas shall be covered or otherwise protected during laser operation. The following guidelines are suggested for maximum eye protection.

- Whenever possible confine (enclose) the beam and provide non-reflective, nonflammable beam stops, to minimize the risk of accidental exposure or fire. Use fluorescent screens or secondary viewers to align the beam; avoid direct beam exposure to the eyes.
- Use the lowest power possible for beam alignment procedures. Use lower class lasers for preliminary alignment procedures, whenever possible. Keep optical benches free of unnecessary reflective items.
- Confine the beam to the optical bench unless necessary for an experiment, e.g., use barriers at side of benches or other enclosures. Do not use room walls to align Class 3b or 4 laser beams.
- Use non-reflective tools. Remember that some tools seem to be non-reflective for visible light, but may be reflective in the invisible part of the spectrum.
- Do not wear reflective jewelry when working with lasers. Metallic jewelry also increases electrocution hazards.

Wear protective glasses whenever working with Class 4 lasers with open beams or when unblocked reflections can occur. This is especially important when working with infrared beams (such as the Nd:YAG fundamental), since the unblocked reflections cannot be seen, and are therefore difficult to locate and block.

Generally, protective eyewear may be selected to be adequate to protect against stray reflections. Wearing such glasses allows some visibility of the beam, preventing skin burns, making it more likely that persons will wear the eye protection. Also, the increased visibility afforded by this level of protection decreases potential for other accidents in the lab, i.e., tripping, etc.

Factors to consider in selection of Laser Protective eyewear include the following:

- Wavelength(s) or spectral region(s) of laser radiation
- Optical density at the particular wavelength(s)
- Maximum irradiance (W/cm²) or beam power (W)
- Type of laser system
- Power mode, single pulse, multiple pulse, or cw

- Possibilities of reflections, specular and diffuse
- Field of view provided by the design
- Availability of prescription lenses or sufficient size of goggle frames to permit wearing of prescription glasses inside of goggles.
- Comfort
- Ventilation ports to prevent fogging
- Effect upon color vision
- Impact resistance
- Ability to perform required tasks while wearing eyewear

Since laser protective eyewear is subject to damage and deterioration, the lab safety program should include periodic inspection of these protective items.

Engineering Controls for Laser Systems

In the Morse group, lasers shall not be modified to defeat the engineering safeguards without review and approval of the PI, or other authorized personnel, to ensure that appropriate controls are instituted.

Appropriate design standards for laser system are as follows:

- Laser should be equipped with a protective housing, an aperture that is clearly identified, and a clearly marked switch to deactivate the laser or reduce its output to less than maximum permissible exposure (MPE). If this is not possible, Radiation Safety should be consulted to assess the hazards and to ensure that appropriate controls are in place. Such controls may include, but are not limited to the following:
 - Access restriction
 - Eye protection
 - Barriers, shrouds, beam stops, etc.
 - Administrative and/or procedural controls
 - Education and training
- Protective housings should be interlocked for Class 3a, 3b and 4 lasers.
- A keyed master switch or password protected operating computer should be provided for Class 3b and 4 lasers. Lasers should be disabled by removing the key when the laser is not in use for prolonged periods.
- Viewing ports and collecting optics shall provide adequate protection to reduce exposure at viewing position to below the MPE level. (Classes 2, 3a, 3b, or 4).
- If the beam path is not enclosed, then the Nominal Hazard Zone (NHZ), the areas where the exposure level exceeds maximum permissible exposure level, need to be assessed and a controlled area established.
- Commercially manufactured Class 3b and Class 4 lasers must come equipped with a connection for external interlocks.
- Laser beams should be terminated in a suitable "beam stop." Most laser heads come equipped with a permanently attached stop or attenuator, which will lower the beam power to less than the MPE at the aperture from the housing. Additional beam stops may be needed in the beam path to keep the useful beam confined to the experimental area.

Control of Laser Areas

In the Morse group, laser labs are to be locked when lasers are operating, with warning signs on the doors. Only personnel who have received laser training in the group will be issued keys to these laboratories. Laser beams will be restricted so that they never are accessible within a minimum distance of 6 feet from the door. Windows into laser labs will be blocked with opaque materials.

For Class 4 lasers that have open beams, the ANSI Standards call for interlocked doors or devices that turn-off or attenuate the laser beam in the event of an unexpected entry into an area. An alternative method of protection is to provide a suitable barrier (screen or curtain) just inside the door or wherever most appropriate to intercept a beam or scatter so that a person entering the room cannot be exposed above the MPE limits. In the Morse group, a barrier will be present to prevent laser beams (and reflected beams) from reaching the doorway area.

Other conditions related to control of laser areas include the following:

- Never direct the laser beam toward the entry.
- Use shields and barriers around the laser work area so that the beam, reflections and scatter are contained on the optical table. Try to keep the unenclosed beam path out of the normal eye-level zone. (The normal eye-range is from 4 to 6 feet from the floor.)
- Ensure that only diffuse reflection materials are in or near the beam path to minimize the chance of specular reflections. When this is not possible, locate and block all specular reflections with suitable beam blocks.
- Ensure that locks or interlocks do not prevent rapid egress from the area in the event of an emergency situation.

Unauthorized persons are to be prevented from entering the laboratories by keeping the doors closed and locked when the lasers are in use. The locks on the doors will be such that they do not impede egress from the laboratory.

Posting and Warning Systems for Laser Controlled Areas

Entrances to laser areas are to be posted in accordance with ANSI Z136.1-2000. In particular, areas where Class 3b or 4 lasers are used must be secured against persons accidentally being exposed to beams, and be provided with a proper warning indication. All windows, doorways, and portals should be covered or restricted to reduce transmitted laser levels below the MPE.

Personnel who do not read the English language, and who may need to enter areas where lasers are used are to be given appropriate instruction as to the meaning of warning signs and labels.

All visitors to the operating laser labs will be escorted by trained personnel while in the lab, in order to keep them safe at all times.

<u>Training</u>

Only qualified and trained employees may operate Class 3b and 4 lasers. To be qualified, a laser operator must meet the training requirements outlined below. The Principal Investigator (Dr. Morse) is responsible for ensuring that all persons who work in areas where Class 3b or 4 lasers are used are provided with appropriate training and written safety instructions (work rules), so that the workers can properly utilize equipment and know and follow safety procedures.

For personnel who work with Class 3b and 4 lasers, the training will included the following topics:

- The biological effects of laser radiation
- The physical principles of lasers
- Classification of lasers
- Basic safety rules
- Use of protective equipment
- Control of related hazards including electrical safety, fire safety, and chemical safety
- Emergency response procedures

All alignment, operation, and maintenance procedures are to be trained by a qualified employee or learned by studying the respective laser manuals.

Because of the hazard of electrocution, it is a recommendation that the lab personnel take a course in cardiopulmonary resuscitation (CPR) and proper rescue techniques to follow in the event of electrocution.

An employee already qualified and trained with the laser system(s) must train any non-University personnel that may need to work on/with Class 3b or 4 lasers. A qualified employee will also closely supervise these individuals until they are comfortable with their level of expertise.

III. Working with Gas Cylinders (Saouma Group)

Standard Operating Procedure

Task: Gas Cylinders Created by: Saouma Group Date: 05/08/2017 Revision Date (Author): Moumita Bhattacharya 05/09/2017

Training Requirements:

- ✓ Department of Chemistry Safety Training
- ✓ Saouma Group Safety Training
- ✓ Fully read and understand this SOP
- ✓ Checked out by a senior lab member that is trained in using gas cylinders

Potential Hazards:

- Falling gas cylinders
- High pressure gases
- Potential toxic/flammable gases
- Fire (flammable gases)
- Stripping (tank or regulator)

Special PPE Requirements:

• Labcoat, safety glasses, nitrile gloves

Materials Needed:

- Wrench
- Gas cylinder cart
- Straps
- Teflon tape
- Regulator
- Hoses, adapters, etc.
- Alligator clips for grounding (flammable gases)



Background:

- Users should understand basic regulator operation before manipulating gases at high pressure.
- The user should be familiar with the markings on the gas cylinder. The top mark is either a DOT or an <u>International Code Council</u> (ICC) marking indicating pertinent regulations for that cylinder. The second mark is the serial number. Under the serial number is the symbol of the manufacturer, user or purchaser. Of the remaining marks the numbers represent the date of manufacture, and retest date (month and year). A (+) sign indicates the cylinder may be 10% overcharged, and a star indicates a ten-year test interval.



Procedure:

Regulator Information

- Check the CGA numbers on *both* the cylinder and the regulator to make sure that they match. This number is usually printed on the flat portion of the cylinder directly below the valve. On most regulators, the number can be found printed on the regulator nut or underneath the dials. Note, NEVER use a regulator that is incompatible with the gas you are using.
- The cylinders and regulators for flammable gasses are reverse threaded to ensure that they are only used together. Usually, the nuts on these regulators are notched to indicate this.
- Common CGA numbers are in the table below. If a gas or gas mixture is not listed, refer to supplier to confirm the CGA number.

CLIARTIC		CCA Einiana				
Required	Pure Gases	Required	Minor Component	xea G	Major Component	
510/300	Acetylene	240/660/705	Ammonia		Nitrogen	
590/346/347/702	Air	350	Rutana	+	Nitrogan	
240/660/705	Ammonia	350	Dutane	-	i viilogen	
580/680/677	Argon	296	Carbon Dioxide		Oxygen	
350	Arsine*	580	Carbon Dioxide		Helium or Nitrogen	
320	Carbon Dioxide	580	Carbon Dioxide Helium			
350	Carbon Monoxide	590	and/or Nitrogen	+	Air	
660	Chlorine	390	Carbon Monoxide	_	Au	
510	Cyclopropane	330	Chlorine		Nitrogen	
350	Deuterium	350 Diborane			Argon, Helium,	
350	Ethane	580	Freon-12	+	Nitrogen	
350	Ethylene	296	Halium	+	Orenan	
510	Ethylene Oxide	290	ricium Oxygen		Oxygen	
580/680/677	Helium	350	Hexane Nitrogen		Nitrogen	
350/695/703	Hydrogen	350	Isobutane		Nitrogen	
330	Hydrogen Chloride	580	Krypton		Argon	
330	Hydrogen Sulfide	590	Methane		Air	
580	Krypton	580	Moisture	+	Argon, Helium or Nitroger	
350/695/703	Methane	660	Nitric Oxide	+	Nitrogen	
510	Methyl Chloride	660	Nimer Divide	+	Ale of Niesson	
580/680/677	Neon	600	Nitrogen Dioxide	_	Air or Nitrogen	
580/680/677	Nitrogen	590	Nitrous Oxide		Nitrogen	
326	Nitrous Oxide	590	Oxygen		Nitrogen or Helium	
540/577/701	Oxygen*	350	Propane		Nitrogen or Helium	
350	Phosphine	590	Propane	+	Air	
510	Propane	660	Sulfur Dioxide	+	Air or Nitrogen	
350	Silane*	590	Sulfur Heraflourid-	+	Armon Helium or Niresson	
668/660	Sulfur Dioxide	390	Sanur riexanouride	_	ragon, rienum or Nitroge	

• For lecture bottles: CGA 170 (non-corrosive) or CGA 180 (corrosives).

Attaching a Regulator

- Make sure that the threads of both the regulator and the cylinder are free of Teflon tape and debris.
- Unless specifically noted, apply one complete wrap of new Teflon tape to the exposed threads in the direction of the thread.
- Tighten the nut while supporting the weight of the regulator. With your fingers. It should travel smoothly as long as the threads are matching correctly. Remember, righty tighty, lefty loosy. (reverse threads are opposite).
- Use a wrench to fully tighten the nut (usually another 1/4 to 1/2 turn).
- If the regulator has not been used recently, or you are unsure of the pressure setting, turn the regulator dial all the way to the left so that it will be set to its lowest pressure delivery setting.

Leak Testing

- Once the regulator is attached, it should be leak tested. One simple method is to use an electronic leak detector. This is located in room 4163.
- Make sure that all tank and regulator valves are closed before you begin.
- If working with a flammable or toxic gas, ensure that the cylinder is in a well ventilated area and if applicable, that the person is wearing a detector.
- Turn on the leak detector and wait for it to equilibrate (about 10 seconds, light will shine a steady green).
- Open the tank valve on top of the cylinder. The cylinder pressure gauge should increase to ~ 2000 psi for most full cylinders. The delivery pressure gauge should read 0 psi. Make a note of the pressure a piece of tape is a good method.
- Inspect the joint between the tank and regulator using the black and yellow probe. The detector will show red dots if a leak is detected; the number of dots corresponds to the severity of the leak.
- Open the regulator dial. Using the detector, inspect the connection and all local joints. Repeat for the delivery valve.
- If a leak is detected, try re-assembling the regulator using Teflon tape, if applicable.
 - Note, it an uncontrolled leak occurs that cannot be contained, contact OEH&S immediately!



- If you are working with a flammable gas, ground the cylinder by attaching one end of an alligator clip (we have used a piece of Cu wire) to the regulator and another end to the metal around a hood (or a cylinder rack).
- Make sure to have a hose attached from the regulator that can then attach to your application.
- Once you know that there are no leaks between the regulator and the cylinder, open the *cylinder valve* fully.
- Adjust the delivery pressure, if necessary, by turning the regulator dial. Clockwise turns increases the pressure while counterclockwise turns decrease the pressure.
 Note, in a closed system, you can only increase the pressure- you can only decrease the pressure once you vent the system or start flowing gas.
- Slowly open the delivery valve to introduce gas to your system. Once flow is established, adjust the delivery valve to attain the desired flow rate. You may need to readjust the delivery pressure.
- For long-term applications, whereby gas is flowing for extended periods of time, both the tank pressure and the delivery pressure should be monitored occasionally. The tank pressure will steadily drop as the gas is depleted, which will impact the delivery pressure. **Note**, two-stage regulators are relatively unaffected by drops in tank pressure, but single-stage regulators will have a significant change in delivery pressure as the tank depletes.
- When done, close the *cylinder valve*.

Removing a Regulator

- Only remove regulators when the tank is not in use, and the *cylinder valve* is shut.
- Be sure to purge any residual gas into a hood (esp. if toxic, like CO): once the *cylinder valve* is closed, vent the residual gas through a bubbler or hose leading into a hood. The pressure gauge should read 0 psig for both cylinder and delivery pressure.
- Close the *delivery valve*.
- Using a wrench, loosen the regulator nut that connects the regulator to the tank. If there is any residual pressure in the regulator you will hear a hiss as the gas is released.
- Once loosened, untighten the regulator from the cylinder by hand. Take care to support the weight of the regulator with your hands, to minimnize the risk of stripping.
- Cap the cylinder, and put the regulator away.

Moving Cylinders

- Cylinders can only be moved when properly capped! If a regulator must remain attached, then a special regulator protector safety cap must be installed.
- Bring the gas cylinder cart next to the cylinder you want to move.
- Unstrap the cylinder and carefully roll it onto the gas cylinder cart.
- Secure the cylinder with the chain, and move the cylinder to its storage area.
- Carefully tip the cart, unstrap the cylinder, and roll the cylinder to its storage location.
- Double strap the cylinder.

If the cylinder is empty, promptly take it to the stockroom. If after hours, mark the cylinder with the letters "MT" or word "empty" and take it down the following day.

<u>Storage</u>

- When not in use, the cylinder must be stored with a cap and no regulator. It should be double strapped to a cylinder rack.
- If you have to use a cylinder and there is no nearby rack, you can either keep it strapped into the cart, or setup the portable cylinder racks. The cylinders must only be stored in this manner during active use.
- Cylinders should be stored in well ventilated areas, away from sources of heat and electricity.
- Oxygen should be stored away from flammable gases.

References and Related SOPs:

- **Prudent Practices in the Laboratory:** https://www.nap.edu/catalog/12654/prudent-practices-in-the-laboratory-handlingand-management-of-chemical
- Miller Group (UNC) SOP
- Anderson Group (UofU) SOP

IV. Working with Cryogenics (Saouma Group)

Standard Operating Procedure

Task: Cryogenics Created by: Saouma Group Date: 05/11/2017 Revision Date (Author): <<Date (Author)>>

Training Requirements:

- ✓ Department of Chemistry Safety Training
- ✓ Saouma Group Safety Training
- ✓ Fully read and understand this SOP

Potential Hazards:

- Cold burns/frostbite. Appropriate PPE includes safety googles, lab coats, closed toe shoes, and clothing that covers arms and legs. Insulated gloves which are easily removed can be worn, but are not recommended due to the high risk of cold burns (with liquid nitrogen). Likewise latex or nitrile gloves can capture splashes of cryogens and hold them close to the skin causing burns as the liquid expands as it warms.
- *Asphyxiation*. Inadequate ventilation poses asphyxiation hazards as oxygen containing air is displaced. Do not use cryogenic fluids in small, closed rooms or rooms with inadequate ventilation.
- *Explosion*. Many cryogenic fluids can condense oxygen from the air to generate liquid oxygen. Liquid oxygen is flammable and explosive; it is characterized by a light, clear blue color. When in combination with organic compounds, the explosive nature of liquid oxygen is exacerbated.
- Pressure build-up. AS fluids warm, they expand, which can result in explosions.
- *Embrittlement*. Materials become more brittle and are prone to breakade when cold.
- Material contraction. Different materials expand at different rates with temperature, so care must be taken to not break equipment upon cooling (or heating). In particular, Schlenk tubes with Teflon plugs should never be fully submerged in cryogenics, as this will result in a leak at the Teflon/glass interface, allowing for air (and oxygen) to enter and condense.

Background:

Cryogenic liquids are fluids with boiling points less than -73°C (-100°F). They are also characterized by a high volume-expansion ratio in the liquid to gas phase. Some physical properties of three reference cryogenic liquids are outlined in the table below.

Identity	Boiling Point	Vapor Pressure (at -196°C)	Volume-Expansion Ratio (at 1 atm, 20°C)
Nitrogen (/)	-195.8°C	730 mm Hg	1:696
Oxygen (/)	-182.9°C	150 mm Hg	1:861
Carbon Dioxide (/)	-78.5°C	1.33 × 10 ^{–8} mm Hg	1:553

Special PPE and Engineering Requirements:

- Labcoat, safety glasses, nitrile gloves
- Face shield (recommended)
- Dish towels (to open/close the IN₂ dewar)

Materials Needed:

- Wrench (for removing hose from IN₂ dewar)
- Blast shield (if suspect liquid oxygen)

Procedure:

IN₂ Dewar: Filling and Transport

- 1. When the large dewar is empty, take a wrench and remove the hose.
- 2. Take the dewar to the elevator, and be sure that the "Do not ride" sign is pointing out.
- 3. Send the elevator down to the stockroom. DO NOT RIDE THE ELEVATOR!
- 4. Go down the stairs with the elevator, ensuring no one gets on. This is easily done with multiple lab members, with someone on each floor. If you are not sure, you can send the elevator down one floor at a time, so you can keep resending it down.
- 5. Take the dewar off the elevator and to the stockroom. Ask them to refill it, and be sure that they give you the BULK price.
- 6. Once it is filled, the stockroom will put it in the hall. **Note**, at this time the dewar is very prone to venting.

- 7. Carefully place the dewar in the elevator, again with the "Do not ride" sticking out. If the dewar starts to vent upon moving, allow it to vent before closing the elevator door.
- 8. Send the dewar up to the fourth floor. As before, you must ensure that no one gets on the elevator.
- 9. Take the elevator to the lab, and tighten the hose with your fingers (do not wrench tighten as the dewar is cold!)

IN₂ Dewar: Taking IN₂

- Never touch any of the valves on the dewar other than that which dispenses. The other valves are for filling and venting, and are safety precautions!
- It is recommended that you use a small towel to handle valves, hoses, etc. that are cold- this minimizes the chance to trap cold close to your skin and cause burns.
- If the dewar begins to hiss, check the gauge- this usually indicates that the dewar is almost empty. If this is the case, then take it down to get refilled.
- 1. Place the small 4 L dewar at the end of the hose, and slowly open the dispensing valve on the dewar. At this time, the hose will "jump" as it is displacing warm air in the dewar (more so if the dewar has not been used in a while).
- **2.** Once the dispensed nitrogen is staying as a liquid, you can slowly increase the flow rate.
- **3.** When you have enough IN_2 , close the value and remove the smaller dewar.

Cold Baths

- When reactions must be run at reduced temperatures, use the appropriate cold bath. You should try to avoid toxic chemicals, and avoid the use of IN₂ if you can.
- See the table below. Note, for temperatures below -77 °C, you must use IN₂ rather than CO₂. Only use high quality IN₂, and ensure that the system remains open.

University of Utah Department of Chemistry Safety Manual 2019

Temperatu	re Composition	Temper	ature Composition
00	Crushed ice		
-5° to -20°	Ice-salt mixtures	-77º	Solid CO ₂ with chloroform or acetone
Up to -20°	Ice-MeOH mixtures	-78º	Solid CO_2 (powdered; CO_2 snow)
-330	Liquid ammonia		
-40° to -50	^o Ice (3.5-4 parts) - CaCl ₂ 6H ₂ O (5 parts)	-100°	Solid CO_2 with diethyl ether
-72°	Solid CO_2 with ethanol	-196º	liquid nitrogen (see footnote*)
Alternatively	the following liquids can be used partial	lv frozen	as cryostats by adding solid CO ₂ from time to
time to the m	aterial in a Dewar-type container and stirr	ing to ma	ke a clush:
130	<i>p</i> -Xylene	-550	Diacetone
120	Dioxane	-560	<i>n</i> -Octane
6º	Cyclohexane	-60°	Di-isopropyl ether
50	Benzene	-730	Trichloroethylene or isopropyl acetate
20	Formamide	-740	<i>o</i> -Cymene or <i>p</i> -cymene
-8.6°	Methyl salicylate	-770	Butyl acetate
_90	Hexane-2.5-dione	-790	Isoamyl acetate
-10.50	Ethylene glycol	-83º	Propylamine
-11.9°	<i>tert</i> -Amyl alcohol	-83.6°	Ethyl acetate
-120	Cycloheptane or methyl benzoate	-86°	Methyl ethyl ketone
-15°	Benzyl alcohol	-89°	<i>n</i> -Butanol
-16.3°	n-Octanol	-90°	Nitroethane
-18 ^o	1,2-Dichlorobenzene	-91°	Heptane
-22°	Tetrachloroethylene	-92°	<i>n</i> -Propyl acetate
-22.4°	Butyl benzoate	-93°	2-Nitropropane or cyclopentane
-22.8°	Carbon tetrachloride	-94°	Ethyl benzene or hexane
-24.5°	Diethyl sulfate	-94.6°	Acetone
-25°	1,3-Dichlorobenzene	-95.1°	Toluene
-29°	o-Xylene or pentachloroethane	-97°	Cumene
-30°	Bromobenzene	-98°	Methanol or methyl acetate
-32°	<i>m</i> -Toluidine	-99°	Isobutyl acetate
-32.6°	Dipropyl ketone	-104°	Cyclohexene
-38°	Thiophene	-107°	Isooctane
-41°	Acetonitrile	-108°	1-Nitropropane
-42°	Pyridine or diethyl ketone	-116 ^o	Ethanol or diethyl ether
-44º	Cyclohexyl chloride	-117º	Isoamyl alcohol
-45°	Chlorobenzene	-126°	Methylcyclohexane
-47º	<i>m</i> -Xylene	-131°	<i>n</i> -Pentane
-50°	Ethyl malonate or <i>n</i> -butylamine	-160°	Isopentane
-52°	Benzyl acetate or diethylcarbitol		

For other organic materials used in low temperature slush-baths with liquid nitrogen see R.E.Rondeau [*J Chem Eng Data* **11** 124 *1966*]. ***NOTE**: Use high quality pure nitrogen; do not use liquid air or liquid nitrogen that has been in contact with air for a long period (due to the dissolution of oxygen in it) as this could EXPLODE in contact with organic matter.

Cold Traps

Appropriate order of operations when using cryogens in cold traps is critical to avoid generating hazards such as condensation of liquid oxygen – an explosion hazard. Cold traps should be checked frequently/re-filled and not left unattended for extended periods of time. When using a cryogenic fluid in a Dewar for use on a vacuum line, it is imperative that the system be under vacuum when the Dewar is set in place. A labelled scheme of a Schlenk line is shown below (Figure 1).



Figure 1: Labelled Scheme of a Schlenk Line.

To put a cryogen filled Dewar on to a schlenk line to create a cold trap, the individual valves (5) and the vent, 4, should be closed before starting. Valve 6 leading to the vacuum gauge and nitrogen bubbler should always be open, unless testing for leaks. Thus, the vacuum manifold should always be under static vacuum. To put up the traps, place a trap lower body/o-ring on the trap upper bottom closest to the vacuum (valve 1). Making sure that valve 2 is closed, valve 1 is then opened. Once you feel that the trap is securely in place and you no longer hear the pump grumbling, clamp the trap (finger tight). This trap is now under dynamic vacuum. With valves 3 and 4 closed, repeat the procedure for the second trap, now opening valve 2 to introduce dynamic vacuum. Finally, open valve 3 to expose you vacuum line/monometer to dynamic vacuum. Note if the mercury level changes0 it shouldn't if your line is holding vacuum. If it doesn't hold vacuum, leak test your line by closing valve 1 and noting any changes in the monometer level (over at least 10 minutes). Once you have established a good dynamic vacuum, place the dewars around the traps, then fill the Dewar with your cryogenic fluid. Check your vacuum gauge and ensure the line is holding vacuum. For most all applications, use liquid nitrogen. The exception is a dry ice/isopropanol mixture for drying celite, sieves, etc.

To remove your Dewars, start by closing the individual valve you were using. Systematically work back toward the pump in the following way: close valve 3 from the main line (creates static vacuum), close valve 2, quickly remove the cryogen filled Dewar, open valve 4 to vent, and carefully remove the cold trap (no longer under vacuum – don't drop it). Then proceed to the next trap: valves 2 and 3 are both closed and valve 4 is still open from the previous step, close valve 1 leading to the pump, remove the Dewar quickly, open valve 2 to the vent, and carefully remove the cold trap. Valve 1 will remain closed and under vacuum leading to the pump.

Important things to remember: never open a cold trap being cooled with a cryogen to the atmosphere as you will condense liquid oxygen (always double check your valves, especially vent valve 4 and individual vales, 5). Always work systematically away from or toward the pump.

A similar flow is used when putting traps on and off of the gloveboxes.

Any extra IN₂ can be put back in the 4L dewar.

Transport

Cryogenic fluids are best kept stored in insulated containers at atmospheric pressure to help keep the liquids near their boiling point. Containers not designed for charge with liquid cryogens should never be used, due to potential pressure building in unvented containers, transfer lines, and pipes from expansion during the liquid to gas transition. The container must also be able to withstand low temperatures without becoming brittle and breaking. Commonly, the Dewar flask is used to store and transfer cryogenic fluids. Considerations when using a Dewar flask include: caps which allow pressure to escape while keeping air and moisture out, charging the flask with transfer tubes designed to withstand cryogenic temperatures, keeping the flask upright, never using a heat gun to warm transfer tubing, protecting the flask's insulating abilities, and placing Dewars on dollies for transport. **You should NEVER ride on an elevator with cryogenics.**

Liquid Oxygen

Liquid oxygen poses a serious danger. While large wuantities of it have a characteristic blue hue to it, do not rely on this hard-to-see color. Most chemicals are solids at liquid nitrogen temperature, so *the presence of any liquid in your traps is cause for alarm*.

If you suspect your cold trap has condensed liquid oxygen, you (and everyone in your vicinity) are in immediate danger. Make sure that the hood sash is down, and that a blast shield is in front of the flask if the operation is not being performed in a hood.

- 1. Notify all lab occupants and your supervisor, and place a blast shield in front of the traps (even if in the hood).
- 2. Inspect the system, taking as many precautions as possible.
- 3. Try to ensure that the liquid nitrogen dewar in which the flask resides has ample liquid nitrogen in order to maintain a temperature of ~ -196 °C. This is to ensure that the Dewars are filled with plenty of cryogen to ensure the liquid oxygen is kept

at an adequately low temperature. Warming of the liquid oxygen could result in pressure buildup and/or a violent oxidation reaction (if organics are present).

- 4. At this stage, you have several options:
 - a. Further venting the system to the open atmosphere is not advised, as this provides an ample supply of oxygen to the system, which may exacerbate the problem. If there are organics present, an explosion may result.
 - b. After ensuring that the dewar is filled with liquid nitrogen, try to locate the leak. If it can be fixed (as in a valve was left open, etc.), quickly seal the leak and put the system under dynamic vacuum (if not already so). If you cannot seal the leak effectively (such as if a valve broke), clear the area immediately and notify your supervisor. Do not re-enter the hood area until the liquid oxygen has been pumped out of the cold trap (this may take several hours).
- 5. Your vacuum gauge/ monometer will indicate if you have fixed the leak and if liquid oxygen has been pumped off (changes by about 100 mm Hg). Evacuate the area. The entire system should be regarded as an explosive danger until no liquid oxygen remains (e.g., the vacuum is returned to its best reading).
- 6. Once the liquid oxygen is removed, get help from your advisor or another qualified researcher. Remove the dewar, then detach the flask from the line and allow it to warm slowly behind a blast shield.

If you suspect your cold trap has condensed liquid oxygen in the presence of an organic compound, the risk and extent of explosion is amplified. Follow the procedure outlined above, and notify the campus emergency service, at 4911. Absolutely ensure all lab occupants are evacuated, and that all entrances to the lab are closed off.

Minimize the risk of liquid oxygen by:

- Never leave a system under static vacuum in a liquid nitrogen bath. A small leak could lead to condensation of liquid oxygen. An active vacuum is required when cooling with liquid nitrogen so that any oxygen that leaks into the system is efficiently removed.
- Use dry ice/acetone when possible, such as when you are drying sieves.
- Regularly check your line for leaks. Do not assume new glasswear is void of leaks, as pinholes may be present. Therefore it is important to always test your glassware for leaks.
- Have a contingency plan for power outages. Loss of power to the vacuum pump while the pumps are being coolds with liquid nitrogen is a common source of liquid oxygen. Don't leave traps unattended unnecessarily and drop all traps promptly if a power outage occurs.

References and Related SOPs:

• PP