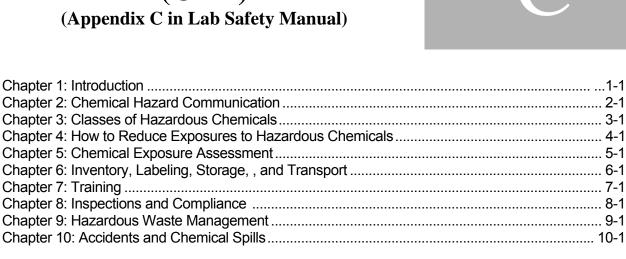
Appendix

Chemical Hygiene Plan (CHP)

(Appendix C in Lab Safety Manual)



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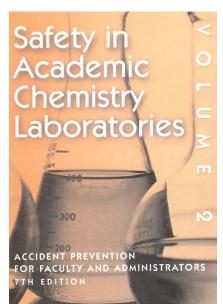
Chapter 1: Introduction

Purpose

The University of California (UC) is committed to providing a healthy and safe working environment for the campus community, free from recognized hazards in accordance with UC Policy

(http://www.ucop.edu/ucophome/coordrev/policy/PP102805_HS E.pdf) and UCI Policy

(http://www.policies.uci.edu/adm/pols/903-10.html). The Chemical Hygiene Plan (CHP) establishes a formal written program for protecting laboratory personnel against adverse health and safety hazards associated with exposure to potentially hazardous chemicals and must be made available to all employees working with hazardous chemicals. The CHP describes the proper use and handling practices and procedures to be followed by faculty, staff, students, visiting scholars, and all other personnel working with potentially hazardous chemicals in laboratory settings. This plan is based on best practices identified in, among others sources, "Prudent Practices for Handling Hazardous Chemicals in Laboratories,"



published by the National Research Council, and the American Chemical Society's "Safety in Academic Chemistry Laboratories" (*www.acs.org*), a copy of which has been distributed along with this manual.

Scope

The CHP applies to all laboratories that use, store or handle potentially hazardous chemicals and all personnel who work in these facilities. It does not apply to research involving <u>exclusively</u> radiological or biological materials, as these safety procedures and regulatory requirements are outlined in the Radiation Safety Manual (http://www.ehs.uci.edu/programs/radiation/RadiationSafetyManual.pdf) and Biosafety Manual (http://www.ehs.uci.edu/programs/biosafety/BiosafetyManual.pdf), respectively. Research involving more than one type of hazard must comply with all applicable regulatory requirements and follow guidance outlined in the relevant safety manuals.

The information presented in the CHP represents best practices and provides a broad overview of the information necessary for the safe operation of laboratories that utilize potentially hazardous chemicals. It is not intended to be all inclusive. Departments, divisions or other work units engaged in work with potentially hazardous chemicals that have unusual characteristics, or are otherwise not sufficiently covered in the written CHP, must customize the document by adding additional sections addressing the hazards and how to mitigate their risks, as appropriate. Such customizations must receive prior approval from the PI/Laboratory Supervisor and/or the Office of Environment, Health and Safety (EH&S). See *Appendix E: Safe Use of Particularly Hazardous Substances* for additional information on substances that may trigger these additions. For information on specific chemical safety topics not covered in the CHP, please contact EH&S, 4-6200.

Implementation of the necessary work practices, procedures, and policies outlined in this CHP is required by the following:

- Title 8, California Code of Regulations (CCR), Section 5191, "Occupational Exposures to Hazardous Chemicals in Laboratories" (http://www.dir.ca.gov/title8/5191.html)
- Title 8, CCR, Section 5209, "Carcinogens" (http://www.dir.ca.gov/title8/5209.html)
- Title 8, CCR, Section 5154.1, "Ventilation Requirements for Laboratory-Type Hood Operations" (http://www.dir.ca.gov/title8/5154_1.html)

Other applicable regulations include those promulgated by the U.S. Department of Labor including 29 CFR 1910.1450 "Occupational Exposure to Hazardous Chemicals in Laboratories" (the "Laboratory Standard"). These regulations require that the CHP be readily available wherever potentially hazardous chemicals are used, handled or stored. EH&S will review and evaluate the effectiveness of this Plan at least annually and update it as necessary.

Completing UCI's Safety-on-Site (SOS) program will satisfy chemical hygiene plan elements.

Rights and Responsibilities

Employees and other personnel who work in laboratories have the right to be informed about the potential health hazards of the chemicals in their work areas and to be properly trained to work safely with these substances. This includes custodial staff and other personnel who work to clean and maintain laboratories. Employees have the right to file a complaint with Cal/OSHA if they feel they are being exposed to unsafe or unhealthy work conditions and cannot be discharged, suspended, or otherwise disciplined by their employer for filing a complaint or exercising these rights. *All personnel working with potentially hazardous chemicals are encouraged to report (anonymously, if preferred) any concerns about unsafe work conditions to EH&S, 4-6200.*

Responsibilities for the health and safety of the campus community extend to the highest administrative levels of UC. The Chancellor and Vice Chancellors are responsible for the implementation of UC's Environmental Health and Safety Policy (http://www.ucop.edu/ucophome/coordrev/policy/PP102805_HSE.pdf) at all facilities and properties under campus control. Deans and Department Heads are responsible for establishing and maintaining programs in their areas and for providing a safe and healthy work environment. (http://www.policies.uci.edu/adm/pols/903-10.html)

While the Chancellor, Vice Chancellors, Deans and Department Heads are responsible for the broad implementation and enforcement of UC's Environmental Health and Safety Policy, the day-to-day responsibility for the management of laboratory safety and adherence to safe laboratory practices rests with the PI/Laboratory Supervisor within individual laboratory units and associated departments. All personnel, including PIs/Laboratory Supervisors, employees, and students, have a duty to fulfill their obligations with respect to maintaining a safe work environment.

All employees and other personnel working with potentially hazardous chemicals have the responsibility to conscientiously participate in training seminars on general laboratory safety and review and be familiar with the contents of the CHP. Those working with chemicals are responsible for staying informed about the chemicals in their work areas, safe work practices and proper personal protective equipment (PPE) required for the safe performance of their job. Failure to comply with these requirements will result in progressive disciplinary action in accordance with UC policy, and may result in temporary suspension of laboratory activities until corrective action is implemented.

Specific duties and responsibilities of personnel who work in areas where potentially hazardous chemicals are present have been compiled in the document entitled General Rules for Laboratory Work with Chemicals, found in *Appendix A*.

RESPONSIBILITIES OF PRINCIPAL INVESTIGATOR (PI)/ LABORATORY SUPERVISOR

The PI/Laboratory Supervisor has responsibility for the health and safety of all personnel working in his or her laboratory who handle hazardous chemicals. The PI/Laboratory Supervisor may delegate safety duties, but remains responsible for ensuring that delegated safety duties are adequately performed. The PI/Laboratory Supervisor is responsible for:

- 1. Knowing all applicable health and safety rules and regulations, training and reporting requirements and standard operating procedures associated with chemical safety for regulated substances;
- 2. Identifying hazardous conditions or operations in the laboratory or other facility containing hazardous chemicals and determining safe procedures and controls, and implementing and enforcing standard safety procedures;
- 3. Establishing standard safety operating procedures (general and protocol specific) and performing literature searches relevant to health and safety for laboratory-specific work;
- 4. Providing prior-approval for the use of hazardous chemicals in the PI/Laboratory Supervisor's laboratory or other facility with hazardous chemicals;
- 5. Consulting with EH&S and/or Departmental Safety Committee on use of higher risk materials, such as use of particularly hazardous substances, as defined by UCI Guidelines, or conducting higher risk experimental procedures so that special safety precautions may be taken;
- 6. Maintaining an updated chemical inventory for the laboratory or facility;
- 7. Ensuring laboratory or other personnel under his/her supervision have access to and are familiar with the appropriate Safety Manual(s);
- 8. Training all laboratory or other personnel he/she supervises to work safely with hazardous materials and maintain written records of laboratory-specific or other specialized training in the lab's Safety on Site Binder(s). Electronic records of training are encouraged. Training must include information of the location and availability of hazard information;
- 9. Promptly notifying EH&S and/or Facilities Management should he/she become aware that work place engineering controls (e.g., fume hoods) and safety equipment (e.g., emergency showers/eyewashes, fire extinguishers, etc.) become non-operational;
- 10. Ensuring the availability of all appropriate personal protective equipment (PPE) (e.g., laboratory coats, gloves, eye protection, etc.) and ensuring the PPE is maintained in working order;
- 11. Conducting periodic self-inspections of laboratory or facility and maintaining records of inspections, as required;
- Promptly reporting of accidents and injuries to EH&S. Serious injuries MUST be reported to EH&S immediately to allow for compliance within the CAL/OSHA 8-hour reporting time frame. Any doubt as to whether an injury is serious should favor reporting;
- 13. Provide funding for medical surveillance and/or medical consultation and examination for laboratory and other personnel, as required;
- 14. Informing facilities personnel, other non-laboratory personnel and any outside contractors of potential laboratory-related hazards when they are required to work in the laboratory environment; and

15. Identifying and minimizing potential hazards to provide a safe environment for repairs and renovations.

Completing the above satisfies elements in the UCI Safety-on-Site (SOS) program.

RESPONSIBILITIES OF ALL PERSONNEL WHO HANDLE POTENTIALLY HAZARDOUS CHEMICALS

All personnel in research or teaching laboratories that use, handle or store potentially hazardous chemicals are responsible for:

- 1. Reviewing and following requirements of the CHP and all appropriate Safety Manuals/Guidelines and Policies;
- 2. Following all verbal and written laboratory safety rules, regulations, and standard operating procedures required for the tasks assigned;
- 3. Developing good personal chemical hygiene habits, including but not limited to, keeping the work areas safe and uncluttered;
- 4. Planning, reviewing and understanding the hazards of materials and processes in their laboratory research or other work procedures prior to conducting work;
- Utilizing appropriate measures to control identified hazards, including consistent and proper use of engineering controls, personal protective equipment, and administrative controls;
- 6. Understanding the capabilities and limitations of PPE issued to them;
- 7. Gaining prior approval from the Pl/Laboratory Supervisor for the use of restricted chemicals and other materials;
- Consulting with PI/Laboratory Supervisor before using these particularly hazardous substances (PHS), explosives and other highly hazardous materials or conducting certain higher risk experimental procedures;
- 9. Immediately reporting all accidents and unsafe conditions to the PI/Laboratory Supervisor;
- 10. Completing all required health, safety and environmental training and providing written documentation to their supervisor;
- 11. Participating in the medical surveillance program, when required;
- 12. Informing the PI/Laboratory Supervisor of any work modifications ordered by a physician as a result of medical surveillance, occupational injury or exposure; and
- 13. When working autonomously or performing independent research or work:
 - a. Reviewing the plan or scope of work for their proposed research with the Pl/Laboratory Supervisor
 - b. Notifying in writing and consulting with the PI/Laboratory Supervisor, in advance, if they intend to significantly deviate from previously reviewed procedures (Note: Significant change may include, but is not limited to, change in the objectives, change in PI, change in the duration, quantity, frequency, temperature or location, increase or change in PPE, and reduction or elimination of engineering controls.)
 - c. Preparing SOPs and performing literature searches relevant to safety and health that are appropriate for their work; and
 - d. Providing appropriate oversight, training and safety information to laboratory or other personnel they supervise or direct.

Completing the above satisfies elements in the UCI Safety-on-Site (SOS) program.

RESPONSIBILITIES OF EH&S AND CHEMICAL HYGIENE OFFICER (CHO)

EH&S is responsible for administering and overseeing institutional implementation of the Laboratory Safety Program. The campus Chemical Hygiene Officer (CHO), Rebecca Lally, is designated by EH&S, and is qualified by training and experience, to provide technical guidance in the development and implementation of the provisions of the Chemical Hygiene Plan. In case of life safety matters or imminent danger to life or health, the Director of EH&S or designee has the authority to order the cessation of the activity until the hazardous condition is abated. EH&S provides technical guidance to personnel at all levels of responsibility on matters pertaining to laboratory use of hazardous materials. The CHO is a member of EH&S and, with support from other EH&S personnel, is responsible for:

- 1. Informing Pls/Laboratory Supervisors of all health and safety requirements and assisting with the selection of appropriate safety controls, including laboratory and other workplace practices, personal protective equipment, engineering controls, training, etc.;
- 2. Conducting periodic inspections and immediately taking steps to abate hazards that may pose a risk to life or safety upon discovery of such hazards;
- 3. Performing hazard assessments, upon request;
- 4. Maintaining area and personal exposure-monitoring records;
- 5. Helping to develop and implement appropriate chemical hygiene policies and practices;
- Having working knowledge of current health and safety rules and regulations, training, reporting requirements and standard operating procedures associated with regulated substances. Such knowledge may be supplemented and developed through research and training materials;
- 7. Working with research staff to review existing SOPs and assist with developing new SOPs for handling hazardous chemicals;
- 8. Providing technical guidance and investigation, as appropriate, for laboratory and other types of accidents and injuries;
- 9. Helping to determine medical surveillance requirements for potentially exposed personnel;
- 10. Reviewing plans for installation of engineering controls and new facility construction/renovation, as requested;
- 11. Reviewing and evaluating the effectiveness of the CHP at least annually and updating it as appropriate

Chapter 2: Chemical Hazard Communication

UC has an established Hazard Communication Program that complies with 8 CCR 5194 (*http://www.dir.ca.gov/title8/5194.html*), the Cal/OSHA Hazard Communication Standard. The purpose of UC's Hazard Communication Program is to ensure that all employees and, upon request, their personal physicians, have the right to receive information regarding the hazardous substances to which they may have been exposed at work. UC is responsible for providing information about the hazardous substances in our workplace, the associated hazards, and the control of these hazards, through a comprehensive hazard communication program that is summarized briefly below. The requirements of the Hazard Communication Program apply to laboratory environments at UC due to the potential for large scale experiments and for activities that may occur outside of areas where engineering controls are available. Proper hazard communication involves the active participation of the PI/Laboratory Supervisor, the EH&S Chemical Safety Officer, and the Laboratory/Facility Safety Coordinator, who are each responsible for providing consultation and safety information to employees working with hazardous chemicals.

List of Hazardous Substances

All labs are required to keep an updated copy of their chemical inventory on file, which must be made available to EH&S upon request. For each hazardous substance on their inventory, specific information on any associated health or safety hazards must be made readily available to all laboratory personnel. Compressed gases need to be included in the inventory list.

Hazard Determination

Pls/Laboratory Supervisors are responsible for verifying if any items on their chemical inventory are subject to the requirements of the hazard communication regulation.

The term "hazardous substance" refers to any chemical for which there is statistically significant evidence based on at least one study conducted in accordance with established scientific principles that acute or chronic health effects may occur in exposed individuals. Hazardous substances include, but are not limited to, those chemicals listed in the following:

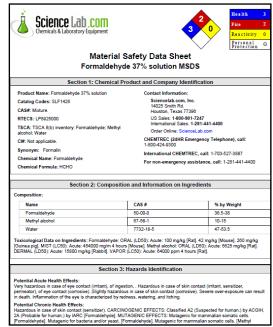
- 1. "The Hazardous Substance List", commonly known as the Directors List of Hazardous Substances, 8 CCR 339 (*http://www.dir.ca.gov/title8/339.html*);
- 2. "Toxic and Hazardous Substances, Air Contaminants", 8 CCR, Section 5155 (*http://www.dir.ca.gov/title8/5155.html*);
- 3. "Threshold Limit Values for Chemical Substances in the Work Environment", ACGIH, 2012;
- 4. "Twelfth Annual Report on Carcinogens", NTP, 2011;
- 5. "Monographs", IARC, WHO (http://www.iarc.fr/en/publications/list/monographs);
- 6. SDSs for reproductive toxins and cancer causing substances (http://www.ehs.uci.edu/msds.html); and
- 7. "Chemicals Known to the State to Cause Cancer or Reproductive Toxicity" (Proposition 65), 22 CCR 12000.

Inventory items found on the above lists are subject to the requirements outlined below.

SAFETY DATA SHEETS (SDS)

A SDS (formerly known as MSDS) must be available for each hazardous substance in a laboratory's chemical inventory. SDSs are available from the UC online SDS available the UC website: library. on (http://www.ehs.uci.edu/msds.html) Pls/Laboratory Supervisors are responsible for keeping SDSs current and making them available to all laboratory employees throughout the work day. SDSs must be in a central location that can be accessed immediately in the event of an emergency. Electronic copies may be kept in a file on a group drive, or hard copies maintained in a central location in the laboratory.

New chemical substances synthesized or produced in a laboratory, and used or shared outside of a laboratory suite, require the preparation of an SDS for each synthesized substance. The UC-system wide SDS library has the capability of developing new SDSs based on the known chemical and physical properties of that substance. Contact EH&S, 4-6200 for more information on preparing new SDSs.



A sample SDS and information on its contents is available in Appendix B.

LABELS AND OTHER FORMS OF WARNING

Labeling requirements for all hazardous substances are summarized as follows:

- All containers of hazardous materials must be labeled with the identity of the hazardous substance
- The label must contain all applicable hazard warning statements
- The name and address of the chemical manufacturer or other responsible party must be present
- Manufacturer's product labels must remain on all containers, and must not be defaced in any way. Appropriate hazard warning statements and Proposition 65 warnings must be present, if not that information must be added
- Labels must be legible, in English, and prominently displayed
- Symbols and/or other languages are required for non-English speaking employees
- Secondary containers (such as spray bottles) must be labeled with the identity of the substance and appropriate hazard warnings
- New synthesized compounds must be labeled with the appropriate hazard warnings based on the knowledge of the chemical and physical properties of that substance.

Additional information on container labeling is provided in Appendix C.

EMPLOYEE INFORMATION AND TRAINING

Employee training on specific workplace hazards must be provided at the time of initial assignment, whenever a new hazard is introduced into the workplace, and whenever employees may be exposed to hazards in other work areas (http://ehs.uci.edu/SafetyTrainingSelf-AssessmentInstructions.pdf). General Hazard Communication Training is available online through the Safety Training module (http://www.uclc.uci.edu/). The online Safety Training is not a substitution for Laboratory Safety Fundamentals Concepts (see Chapter 7). Additional employee training is required whenever a new hazard is introduced into the work environment, and must be provided within 30 days of receiving the SDS or other safety information. All training must be in the appropriate language, educational level, and vocabulary for laboratory personnel. Employees must be given the opportunity to ask questions.

LABORATORY PPE HAZARD ASSESSMENT TOOL

The Laboratory Personal Protective Equipment (PPE) Hazard Assessment Tool, found at http://www.ehs.uci.edu/PPE.html was developed to broadly identify activities involving chemical and other types of hazards and is an effective method of hazard communication. The Laboratory Personal Protective Equipment (PPE) Hazard Assessment Tool captures information on the specific type of hazard(s), the location of the hazard(s), the name of the Pl/Laboratory Supervisor who oversees the facility and helps identify the proper PPE that should be used by laboratory personnel to protect themselves against these hazards. Once the required PPE is identified, the laboratory is required to conduct and document training for laboratory personnel on the use of PPE.

Other Resources

- 1. "Occupational Exposure to Hazardous Chemicals in Laboratories." California Code of Regulations (CCR) Title 8, Section 5191;
- 2. Standard Operating Procedures (SOPs) for handling toxic chemicals (Appendices D, P through Y);
- 3. General information on the signs and symptoms associated with exposure to hazardous substances used in the laboratory or facility
 - Identity labels, showing contents of containers (including waste receptacles) and associated hazards;
 - Label hazardous waste containers. See the UCI EH&S website for hazardous waste management information (http://www.ehs.uci.edu/programs/enviro/index.html);
 - Warnings at areas or equipment where special or unusual hazards exist (e.g., particularly hazardous substances);
- 4. Procedures to follow in case of an emergency; including the posting of the "UCI Injuries and Medical Treatment" poster (http://ehs.uci.edu/MedEmergPoster.pdf)
 - Emergency telephone numbers of emergency personnel/facilities, supervisors, and laboratory workers; and
 - Location signs for safety showers, eyewash stations, other safety and first aid equipment, exits and areas where food and beverage consumption and storage are permitted.
 - Report injury, illness, or safety concern online : https://www.ehs.uci.edu/apps/hr/index.jsp
 - Work related injury and illness information available online: http://snap.uci.edu/viewXmlFile.jsp?resourceID=712)

Chapter 3: Classes of Hazardous Chemicals

Identification & Classification of Hazardous Chemicals

Chemicals can be divided into several different hazard classes. The hazard class will determine how these materials should be stored and handled and what special equipment and procedures are needed to use them safely. For more detailed information on chemical class hazards, please refer to the UCI Laboratory Manual, Appendix E.

Each chemical container, whether supplied by a vendor or produced in the laboratory, must include labels that clearly identify the hazards associated with that chemical. In addition to specific chemical labels, hazard information for specific chemicals can be found by referencing the Safety Data Sheet (SDS) for that chemical.

It is essential that all laboratory workers understand the types of hazards, recognize the routes of exposure, and are familiar with the major hazard classes of chemicals. In many cases, the specific hazards associated with new compounds and mixtures will not be known, so it is recommended that all chemical compounds be treated as if they were potentially harmful and to use appropriate eye, inhalation and skin protection equipment.

FLAMMABILITY HAZARDS

A number of highly flammable substances are in common use in campus laboratories. Flammable liquids include those chemicals that have a flashpoint of less than 100 degrees Fahrenheit. These materials must be stored in flammable storage cabinets in aggregate quantities of 10 gallons or more. Flame-resistant laboratory coats must be worn when working with large quantities (4 liters or more) of flammable materials and/or with procedures where a significant fire risk is present (e.g., when working with open flame, etc.). These materials can constitute a significant immediate threat and should be treated with particular



care, even though the use of these materials is fairly common in the laboratory setting. Particular attention should be given to preventing static electricity and sparks when handling flammable liquids.

REACTIVITY HAZARDS

Reactive and explosive substances are materials that decompose under conditions of mechanical shock, elevated temperature, or chemical action, and release of large volumes of gases and heat. Some materials, such as peroxide formers, may not be explosive, but may form explosive substances over time. These substances pose an immediate potential hazard and procedures which use them must be carefully reviewed. These materials must also be stored in a separate flame-resistant storage cabinet or, in many cases, in laboratory grade refrigerator or freezer that are designed for flammable and reactive chemicals. Pyrophoric chemicals are a special classification of reactive materials that spontaneously combust when in contact with air and require laboratory-specific training. Flame-resistant laboratory coats must always be worn when working with pyrophoric chemicals.

HEALTH HAZARDS

Cal/OSHA uses the following definition for health hazards:

The term 'health hazard' includes chemicals which are carcinogens, toxic or highly toxic agents, reproductive toxins, irritants, corrosives, sensitizers, hepatotoxins, nephrotoxins, neurotoxins, agents which act on the hematopoietic systems, and agents which damage the lungs, skin, eyes, or mucous membranes.



The major classes of "hazardous" and "particularly hazardous substances" and their related health and safety risks are detailed below.

Corrosive Substances

As a health hazard, corrosive substances cause destruction of, or alterations in, living tissue by chemical action at the site of contact.



Major classes of corrosive substances include:

- Strong acids e.g., sulfuric, nitric, hydrochloric and hydrofluoric acids
- Strong bases e.g., sodium hydroxide, potassium hydroxide and ammonium hydroxide
- Dehydrating agents e.g., sulfuric acid, sodium hydroxide, phosphorus pentoxide and calcium oxide
- Oxidizing agents e.g., hydrogen peroxide, chlorine and bromine.

Symptoms of exposure for inhalation include a burning sensation, coughing, wheezing, laryngitis, shortness of breath, nausea, and vomiting. For eyes, symptoms include pain, blood shot eyes, tearing, and blurring of vision. For skin, symptoms may include reddening, pain, inflammation, bleeding, blistering and burns. As a physical hazard, corrosive substances may corrode materials they come in contact with and may be highly reactive with other substances. It is important to review information regarding the materials they may corrode, and their reactivity with other substances, as well as information on health effects. In most cases, these materials should be segregated from other chemicals and require secondary containment when in storage.

Irritants

Irritants are defined as non-corrosive chemicals that cause reversible inflammatory effects on living tissue by chemical action at the site of contact. A wide variety of organic and inorganic compounds, including many chemicals that are in a powder or crystalline form, are irritants. The most common example of an irritant may be ordinary smoke which can irritate the nasal passages and respiratory system. Consequently, eye and skin contact with all laboratory chemicals should always be avoided. Symptoms of exposure can include reddening or discomfort of the skin and irritation to respiratory systems.

Sensitizers

A sensitizer (allergen) is a substance that causes exposed people to develop an allergic reaction in normal tissue after repeated exposure to the substance. Examples of sensitizers include diazomethane, chromium, nickel, formaldehyde, isocyanates, arylhydrazines, benzylic and allylic halides, and many phenol derivatives. Sensitizer exposure can lead to all of the symptoms associated with allergic reactions, or can increase an individual's existing allergies.



Hazardous Substances with Toxic Effects on Specific Organs

Substances included in this category include:

- Hepatotoxins i.e., substances that produce liver damage, such as nitrosamines and carbon tetrachloride
- Nephrotoxins i.e., agents causing damage to the kidneys, such as certain halogenated hydrocarbons
- Neurotoxins i.e., substances which produce their primary toxic effects on the nervous system, such as mercury, acrylamide and carbon disulfide
- Agents which act on the hematopoietic system e.g., carbon monoxide and cyanides which decrease hemoglobin function and deprive the body tissues of oxygen
- Agents which damage lung tissue e.g., asbestos and silica.

Symptoms of exposure to these materials vary. Staff working with these materials should review the SDS for the specific material being used and should take special note of the associated symptoms of exposure.

Particularly Hazardous Substances

OSHA recognizes that some classes of chemical substances pose a greater health and safety risk than others. To differentiate this different risk characteristic, OSHA identifies two categories of hazardous chemicals:

- 1. hazardous chemicals; and
- 2. particularly hazardous substances.

Substances that pose such significant threats to human health are classified as "particularly hazardous substances" (PHSs). The OSHA Laboratory Standard and Cal/OSHA regulation require that special provisions be established to prevent the harmful exposure of researchers to PHSs, including the establishment of designated areas for their use.

See Safe Use of Particularly Hazardous Substances (*Appendix E*) for more information, which also includes a list of common particularly hazardous chemicals used inside laboratories.

Particularly hazardous substances are divided into three primary types:

- 1. Acute Toxins;
- 2. Reproductive Toxins; and
- 3. Carcinogens.

Acute Toxins

Substances that have a high degree of acute toxicity are interpreted by OSHA as being substances that "may be fatal or cause damage to target organs as the result of a single exposure or exposures of short duration." These chemicals, associated chemical waste, and storage containers must be handled with care to prevent cross contamination of work areas and unexpected contact. These chemicals must be labeled as "Toxic." Empty containers of these substances must be packaged and disposed of as hazardous waste without rinsing trace amounts into the sanitary sewer system.

Reproductive Toxins

Reproductive toxins (*http://web.princeton.edu/sites/ehs/labsafetymanual/appa.htm*) include any chemical that may affect the reproductive capabilities, including chromosomal damage (mutations) and effects on fetuses (teratogenesis).

Reproductive toxins can affect the reproductive health of both men and women if proper procedures and controls are not used. For women, exposure to reproductive toxins during pregnancy can 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. For men, exposure can lead to sterility.

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). Pregnant

women and women intending to become pregnant should consult with their laboratory supervisor and EH&S before working with substances that are suspected to be reproductive toxins.

Carcinogens

Carcinogens are chemical or physical agents that cause cancer. Generally they are chronically toxic substances; that is, they cause damage after repeated or long-duration exposure, and their effects may only become evident after a long latency period. Chronic toxins are particularly insidious because they may have no immediately apparent harmful effects. These materials are separated into two classes:

- 1. Select Carcinogens; and
- 2. Regulated Carcinogens.

Select carcinogens are materials which have met certain criteria established by the National Toxicology Program or the International Agency for Research on Cancer regarding the risk of cancer via certain exposure routes. (See definition Select Carcinogen.) It is important to recognize that some substances involved in research laboratories are new compounds and have not been subjected to testing for carcinogenicity. The following references (links provided) are used to determine which substances are select carcinogens by Cal/OSHA's classification:

- OSHA Carcinogen List (http://web.princeton.edu/sites/ehs/labsafetymanual/sec7j.htm)
- Annual Report on Carcinogens published by the National Toxicology Program (NTP), including all of the substances listed as "known to be carcinogens" and some substances listed as "reasonably anticipated to be carcinogens" (http://ntp.niehs.nih.gov/index.cfm?objectid=32BA9724-F1F6-975E-7FCE50709CB4C932)
- International Agency for Research on Cancer (IARC), including all of Group 1 "carcinogen to humans" by the International Agency for Research on Cancer Monographs (IARC) (Volumes 1-48 and Supplements 1-8); and some in Group 2A or 2B, "reasonably anticipated to be carcinogens" by the National Toxicology Program (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 (*http://monographs.iarc.fr/ENG/Classification/crthgr01.php*)

Regulated Carcinogens fall into a higher hazard class and have extensive additional requirements associated with them. The use of these agents may require personal exposure sampling based on usage. When working with Regulated Carcinogens, it is particularly important to review and effectively apply engineering and administrative safety controls as the regulatory requirements for laboratories that may exceed long term (8 hour) or short term (15 minutes) threshold values for these chemicals are very extensive. A complete list of Regulated Carcinogens can be found in *Appendix F*.

Chapter 4: How to Reduce Exposures to Hazardous Chemicals

Introduction

Hazardous chemicals require a carefully considered, multi-tiered approach to ensure safety. There are four primary routes of exposure for chemicals which have associated health hazards (illustrated in Figure 4.1):

- 1. Inhalation;
- 2. Absorption (through the skin or eyes);
- 3. Ingestion; and
- 4. Injection (skin being punctured by a contaminated sharp object or uptake through an existing open wound).

Of these, the most likely route of exposure in the laboratory is by inhalation. Many hazardous chemicals may affect people through more than one of these exposure modes, so it is critical that protective measures are in place for each of these uptake mechanisms.

Safety Controls

Safety controls are divided into three main classifications:

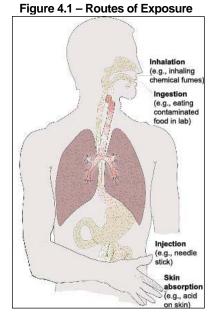
- 1. Engineering Controls;
- 2. Administrative Controls; and
- 3. Protective Apparel and Equipment.

Elements of these three classes are used in a layered approach to create a safe working environment. The principles of each of these elements are detailed below.

ENGINEERING CONTROLS

Engineering controls include all "built in" safety systems. These controls offer the first line of protection and are highly effective in that they generally require minimal special procedures or actions on the part of the user except in emergency situations. A fundamental and very common example is the laboratory fume hood which is very effective at containing chemical hazards and protecting users from inhalation hazards. Other examples of engineering controls include general room ventilation, flammable material storage units, and secondary containment.

General Laboratory Ventilation



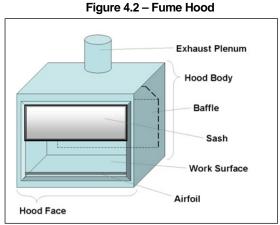
All laboratory rooms in which hazardous materials are used must have fresh air ventilation with 100% of the exhaust venting to the outside; laboratory rooms should not be part of recycled air systems. In cases where this is not desirable, a formal hazard evaluation will be made by EH&S to determine what work can be done in the space and under what special conditions or limitations. Laboratory rooms should be kept at negative pressure compared to public areas to prevent the spread of hazardous vapors. See the University of California Environment, Health and Safety (EH&S) Laboratory Safety Design Guide for additional information on laboratory ventilation.

Fume Hoods

Fume hoods are the most commonly used local exhaust system on campus. Other methods include vented enclosures for large pieces of equipment or chemical

storage, and portable exhaust systems for capturing contaminants near the point of release. Some systems are equipped with air cleaning devices (HEPA filters or carbon absorbers). Exhaust from fume hoods are designed to terminate at least ten feet above the roof deck or two feet above the top of any parapet wall, which ever is higher. Figure 4.2 displays the key components of a fume hood.

It is advisable to use a laboratory hood when working with all hazardous substances. In addition, a laboratory hood or other suitable containment device must be used for all work with "particularly hazardous substances." A properly



operating and correctly used laboratory hood can reduce or eliminate volatile liquids, dusts and mists. Fume hoods are evaluated for operation and certified by EH&S on an annual basis. These annual evaluations check the fume hood air flow velocity to ensure that the unit will contain hazardous vapors. Data on annual fume hood monitoring will be maintained by EH&S. A complete report of fume hood monitoring data must be kept for one year; summary data must be maintained for 5 years.

Each fume hood should have a current calibration sticker and a marker indicating the highest sash height to be used when working with hazardous materials. Contact EH&S for a hood evaluation if these labels are missing.

Each fume hood must be equipped with at least one type of continuous quantitative monitoring device designed to provide the user with current information on the operational status of the hood. Many hoods also have motion sensors to determine when they are not in active use. These sensors will reduce the fume hood's air flow as part of the campus' energy savings effort. When hazardous materials are in a fume hood, but it is not under active use (e.g., during an unattended reaction or experiment), the sash should be closed. Fume hoods are not designed for storage of hazardous materials.

Routine maintenance and repairs of fume hoods are conducted by Facilities Management. However, in most cases, the fume hood must be cleared by EH&S prior to commencement of repairs. The user may initiate the clearance request by completing the online form https://www.ehs.uci.edu/apps/pimoves/index.jsp. The user will receive further instruction after initiating the clearance request. EH&S does not initiate maintenance but will coordinate with Facilities Management to ensure its completion. An electronic notification is generated by Facilities Management after the work order is completed.

General Rules for Fume Hood Use

The following general rules should be followed when using laboratory hoods:

- 1. Fume hoods should not be used for work involving hazardous substances unless they have a certification label that confirms certification has occurred within the past year
- 2. Always keep hazardous chemicals >6 inches behind the plane of the sash
- 3. **Never** put your head inside an operating laboratory hood. The plane of the sash is the barrier between contaminated and uncontaminated air
- 4. Work with the hood sash in the **lowest practical position.** The sash acts as a physical barrier in the event of an accident. Keep the sash closed when not conducting work in the hood
- 5. Do not clutter your hood with unnecessary bottles or equipment. Keep it clean and clear. Only materials actively in use should be in the hood
- 6. Do not make any modifications to hoods, duct work, or the exhaust system without first contacting the EH&S office at your campus.
- 7. Do not use large equipment in laboratory hoods unless the hood is dedicated for this purpose, as large obstructions can change the airflow patterns and render the hood unsafe
- 8. Shut your sash! For energy efficiency, make sure to shut your sash when the hood is not in use

Laboratory fume hoods are one of the most important pieces of equipment used to protect laboratory and other workers from exposure to hazardous chemicals. Chemical fume hoods should be inspected upon installation, renovation, when a deficiency is reported, or a change has been made to the operating characteristics of the hood. Since fume hoods used for regulated carcinogens have additional requirements, such as increased face velocity, contact the *EH&S* office at your campus if the intended use changes.

Fume Hood Inspections		
 Step 1 – Physical Inspection Evaluates the physical condition of the hood and the materials being used in the hood. This includes checking for: Improper storage of materials inside the fume hood Use of proper materials General hood cleanliness Physical damage to the fume hood (e.g., broken sash) Fully functioning lighting, fume hood indicator, airflow monitor, and alarm 	 Step 2 – Hood Performance Inspection Evaluates the overall hood performance to ensure that it is functioning properly. This involves checking the: Average face velocity and set minimum face velocity, which is used to determine the rating of the hood and what the hood can be used for Noise generated by the fume hood, to ensure that it is below 85 dB If fume hood does not pass inspection, it will be labeled with a "DO NOT USE" sign until it can be repaired. 	

Glove Boxes and Ventilation Devices

In addition to fume hoods, some laboratories use contained glove box units for working with reactive chemicals under an inert environment, working with very toxic substances in a completely closed system, or for creating a stable, breeze free, system for weighing hazardous or reactive materials. These units can be very effective because they offer complete containment.

Other Engineering Controls

In addition to the elements listed above, consideration must be given to providing sufficient engineering controls for the storage and handling of hazardous materials. No more than 10 gallons of flammable chemicals may be stored outside of an approved flammable storage cabinet. For refrigerated or frozen storage, flammable and explosive materials must be kept in refrigeration units specifically designed for storing these materials. Generally these units do not have internal lights or electronic systems that could spark and trigger an ignition; additionally, the cooling elements are external to the unit. These units should be labeled with a rating from Underwriters Laboratory or other certifying organization

Secondary containment must be provided for corrosive and reactive chemicals and is recommended for all other hazardous chemicals. Secondary containment should be made of chemically resistant materials and should be sufficient to hold the volume of at least the largest single bottle stored in the container.

Laboratories that use hazardous materials must contain a sink, kept clear for hand washing to remove any final residual contamination. Hand washing is recommended whenever a staff member who has been working with hazardous materials plans to exit the laboratory or work on a project that does not involve hazardous materials.

ADMINISTRATIVE CONTROLS

The next layer of safety controls are Administrative Controls. These controls consist of policies and procedures; they are not generally as reliable as engineering controls in that the user has to carefully follow the appropriate procedures and must be fully trained and aware in order to do so.

EH&S requires that each laboratory have safety procedures, which include safety practices, for any work that involves hazardous materials. In many cases, a general safe operating procedure can be created in consultation with the Departmental Safety Committee, for a class of chemicals that have similar properties. For example, a laboratory group may have one set of safety guidelines for using acids in their laboratory if the acids used have similar properties and/or if the significant differences are delineated in the general procedure. In addition to safety procedures, laboratory groups must submit proposed changes in procedures to the Departmental Safety Committee for review prior to implementation if these changes could pose an additional or significantly greater hazard then the standard procedure. These reviews are especially important in cases where immediate hazards are present such as large quantities of flammable material, explosives or highly reactive material, or highly toxic substances.

Laboratory groups should also review their operations to minimize the amounts of hazardous substances in use or to replace them with less hazardous alternatives. Attention must also be paid to the appropriate segregation of incompatible materials.

Standard Operating Procedures

Standard operating procedures (SOPs) (*Appendices D,P through Y*) or Job Safety Analysis (JSAs) that are relevant to safety and health considerations must be developed and followed when laboratory work involves the use of hazardous chemicals (CCR, Title 8, Section 5191 (e)(3)(A)), especially for "particularly hazardous substances" (PHS). SOPs are written instructions that detail the steps that will be performed during a given experimental procedure and include information about potential hazards and how these hazards will be mitigated. SOPs should be written by laboratory

personnel who are most knowledgeable and involved with the experimental process. The development and implementation of SOPs is a core component of promoting a strong safety culture in the laboratory and helps ensure a safe work environment.

While general guidance regarding laboratory work with chemicals is contained in this plan, Pls/Laboratory Supervisors are required to develop and implement laboratory-specific SOPs for certain hazardous chemicals and PHS that are used in their laboratories. These SOPs must be reviewed by the PI prior to implementation. For certain hazardous chemicals, PHS, or specialized practices, consideration must be given to whether additional consultation with safety professionals is warranted or required.

Circumstances requiring prior approval from the PI/Laboratory Supervisor must also be addressed in laboratory specific SOPs. These circumstances are based on the inherent hazards of the material being used, the hazards associated with the experimental process, the experience level of the worker, and the scale of the experiment. Some examples of circumstances that may require prior approval include working alone in a laboratory, unattended or overnight operations, the use of highly toxic gas of any amount, the use of large quantities of toxic or corrosive gases, the use of extremely reactive chemicals (e.g., pyrophorics, water reactive chemicals), or the use of carcinogens.

UC maintains a website (http://www.ehs.uci.edu/) with tools and resources that may be referenced while developing SOPs, including fact sheets for the use of certain hazardous chemicals, online safety videos and an SOP Library (http://www.ehs.uci.edu/programs/sop_library/index.html) EH&S is also available to assist with the development of SOPs. SOPs must be developed prior to initiating any experiments with hazardous chemicals or PHS and are to be filed and maintained in the Safety on Site binder where they are available to all laboratory personnel.

When drafting an SOP, consider the type and quantity of the chemical being used, along with the frequency of use. The Safety Data Sheet (SDS) for each hazardous chemical or PHS that will be addressed in the SOP should be referenced during SOP development. The SDS lists important information that will need to be considered, such as exposure limits, type of toxicity, warning properties, and symptoms of exposure. If a new chemical will be produced during the experiment, an SDS will not necessarily be available. In these cases, the toxicity is unknown and it must be assumed that the substance is particularly hazardous, as a mixture of chemicals will generally be more toxic than its most toxic component.

PROTECTIVE APPAREL AND EQUIPMENT

Personal Protective Equipment

Personal protective equipment (PPE) serves as a researcher's last line of defense against chemical exposures and is required by everyone entering a laboratory containing hazardous chemicals. Specific minimum requirements for PPE use for chemical operations are determined by the Laboratory Personal Protective Equipment (PPE) Tool at

http://www.ehs.uci.edu/programs/PPE/LabPPEAssessmentTool.doc. (Appendix O). For information on PPE requirements visit the EH&S website at http://www.ehs.uci.edu/PPE.html

The Laboratory PPE Assessment Tool must be completed by the PI, Lab Supervisor, or their designee as a means to conduct a laboratory specific hazard assessment. The laboratory hazard assessment identifies hazards to employees and specifies personal protective equipment (PPE) to protect employees during work activities. PIs/Lab Supervisors are responsible for enforcing PPE

requirements. EH&S personnel are available to assist with completing this form. EH&S may also be consulted by calling 949-824-6200.

The PPE policy outlines the basic PPE requirements, which generally include (as determined by the Laboratory PPE Assessment Tool) but are not limited to:

- Full length pants and close-toed shoes, or equivalent
- Protective gloves, laboratory coats, & eye protection when working with, or adjacent to, hazardous chemicals
- Flame resistant laboratory coats for high hazard materials, pyrophorics, and ≥4 liters of flammables

The primary goal of basic PPE is to mitigate, at a minimum, the hazard associated with exposure to hazardous substances. In some cases, additional, or more protective, equipment must be used. If a project involves a chemical splash hazard, chemical goggles are required; face shields may also be required when working with chemicals that may cause immediate skin damage. Safety goggles differ from safety glasses in that they form a seal with the face, which completely isolates the eyes from the hazard. If a significant splash hazard exists, heavy gloves, protective aprons and sleeves may also be needed. Gloves should only be used under the specific condition for which they are designed, as no glove is impervious to all chemicals. It is also important to note that gloves degrade over time, so they should be replaced as necessary to ensure adequate protection. The EH&S website provides PPE selection guidance (http://www.ehs.uci.edu/PPE.html) to assist in selecting the appropriate PPE for the type of potential hazard.

EH&S requires each laboratory to complete a Laboratory PPE Hazard Assessment prior to beginning work and to provide annual updates thereafter. PPE can be selected based on this hazard assessment. The online Laboratory PPE Hazard Assessment Tool can be accessed at: http://www.ehs.uci.edu/programs/PPE/LabPPEAssessmentTool.doc

How to Use and Maintain PPE

Personal protective equipment should be kept clean and stored in an area where it will not become contaminated. Personal protective equipment should be inspected prior to use to ensure it is in good condition. It should fit properly and be worn properly. If it becomes contaminated or damaged, it should be cleaned or repaired when possible, or discarded and replaced.

For additional requirements and information on selection of PPE, see http://www.ehs.uci.edu/programs/PPE/LabPPEAssessmentTool.doc

Contaminated Clothing/PPE

In cases where spills or splashes of hazardous chemicals on clothing or PPE occur, the clothing/PPE should immediately be removed and placed in a closed container that prevents release of the chemical. Heavily contaminated clothing/PPE resulting from an accidental spill should be disposed of as hazardous waste. Non-heavily contaminated laboratory coats should be cleaned and properly laundered, as appropriate. Laboratory personnel should **never** take contaminated items home for cleaning or laundering. Persons or companies hired to clean contaminated items must be informed of potentially harmful effects of exposure to hazardous chemicals and must be provided with information to protect themselves.

Respiratory Protection

Typically, respiratory protection is not needed in a laboratory. Under most circumstances, safe work practices, small scale usage, and engineering controls (fume hoods, biosafety cabinets, and general ventilation) adequately protect laboratory workers from chemical and biological hazards. Under certain circumstances, however, respiratory protection may be needed. These can include:

- An accidental spill such as:
 - a chemical spill outside the fume hood
 - o a spill of biohazardous material outside a biosafety cabinet
- Performance of an unusual operation that cannot be conducted under the fume hood or biosafety cabinet
- When weighing powdered chemicals or microbiological media outside a glove box or other protective enclosure. Disposable filtering face-piece respirators are generally recommended for nuisance dusts. If the chemicals are toxic, contact EH&S for additional evaluation
- When exposure monitoring indicates that exposures exist that cannot be controlled by engineering or administrative controls
- As required by a specific laboratory protocol or as defined by applicable regulations

Because there are numerous types of respirators available, and each has specific limitations and applications, respirator selection and use requires pre-approval by EH&S. For either required or voluntary use of a respirator, the employee must fill out the Respiratory Hazard Assessment form (*Appendix G*), review it with his/her supervisor, and fax the completed form to EH&S, 4-6200. EH&S will contact the employee to evaluate the potential exposure. The review will include an evaluation of the work area and activities for the following:

- Provision of additional ventilation controls or enclosure of the airborne hazard
- Substitution with a less hazardous substance
- Qualitative or quantitative exposure assessment
- Respirator usage

Tasks with potential airborne hazards that cannot be eliminated by engineering or administrative controls will not be authorized by EH&S until affected employees can be incorporated into UCI's Respiratory Protection Program at http://www.ehs.uci.edu/programs/ih/respiratory.html

If EH&S recommends respirator use for a task, the employee must first enroll in the next available Respirator Training and Fit Testing offered through EH&S. These classes contain the three components required by Cal/OSHA: medical evaluation, training and fit testing. The class schedule is available on the UC Learning Center website (http://www.uclc.uci.edu/). Employees must complete all components prior to starting work that requires respirator use.

Because wearing respiratory equipment places a physical burden on the user, laboratory workers must be medically evaluated prior to wearing respiratory equipment. Certain individuals (e.g., persons with severe asthma, heart conditions, or claustrophobia) may not be medically qualified to wear a respirator. Upon enrollment in Respirator Training and Fit Testing, the employee will be sent the appropriate medical questionnaire. The completed medical questionnaire will be evaluated by a licensed health care professional before the employee proceeds with the training. NOTE: This medical questionnaire is confidential. The employee will be provided additional information on how to contact the licensed health care professional for follow up questions.

After successful completion of the medical evaluation, the employee will be trained and fit tested by EH&S. Training topics include:

- Why the respirator is necessary and how improper fit, usage, or maintenance can compromise the protective effect of the respirator
- What the limitations and capabilities of the respirator are
- How to use the respirator effectively in emergency situations, including situations in which the respirator malfunctions
- How to inspect, put on and remove, use, and check the seals of the respirator
- What the procedures are for maintenance and storage of the respirator
- How to recognize medical signs and symptoms that may limit or prevent the effective use of respirators
- The general requirements of the respiratory program

Finally, a qualitative or quantitative fit test is conducted by EH&S for each respirator user. The fit test ensures a proper face to face piece seal for each individual and his/her mask. Fit testing is done in accordance with UCI's Respiratory Protection Program (http://www.ehs.uci.edu/programs/ih/respiratory.html) and Cal/OSHA regulations (8 CCR 5144) (http://www.dir.ca.gov/title8/5144.html).

An annual refresher is required for the medical evaluation, respirator training, and fit testing. In addition to the annual training refresher, a more frequent re-training, fit testing or medical evaluation must be performed when any of the following occur:

- Changes in the workplace or the type of respirator render previous training obsolete
- Inadequacies in the employee's knowledge or use of the respirator indicate that the employee has not retained the requisite understanding or skill
- Any other situation arises in which reevaluation appears necessary to ensure safe respirator use
- Facial scarring, dental changes, cosmetic surgery, or an obvious change in body weight
- An employee reports medical signs or symptoms related to their ability to use a respirator

Laboratory Safety Equipment

New personnel must be instructed in the location of fire extinguishers, safety showers, and other safety equipment *before* they begin work in the laboratory. This training is considered part of the laboratory specific training that all staff members must attend.

Fire Extinguishers

All laboratories working with combustible or flammable chemicals must be outfitted with appropriate fire extinguishers. All extinguishers should be mounted on a wall in an area free of clutter or stored in a fire extinguisher cabinet. Research personnel should be familiar with the location, use and classification of the extinguishers in their laboratory.

Laboratory personnel are <u>not required</u> to extinguish fires that occur in their work areas and should not attempt to do so unless:

- It is a small fire (i.e., small trash can sized fire)
- Appropriate fire extinguisher training has been received (http://www.uclc.uci.edu/)
- It is safe to do so

Any time a fire extinguisher is used, no matter for how brief a period, the PI/Laboratory Supervisor, or most senior laboratory personnel present at the time of the incident, must immediately report the incident to EH&S.

Safety Showers and Eyewash Stations

All laboratories using hazardous chemicals must have immediate access to safety showers with eye wash stations. Access must be available in **10 seconds** or less for a potentially injured individual and access routes must be kept clear. Safety showers must have a minimum clearance of 16 inches from the centerline of the spray pattern in all directions at all times; this means that no objects should be stored or left within this distance of the safety shower. Sink based eyewash stations and drench hoses are <u>not adequate</u> to meet this requirement and can only be used to support an existing compliant system.

In the event of an emergency, individuals using the safety shower should be assisted by an uninjured person to aid in decontamination and should be encouraged to stay in the safety shower for 15 minutes to remove all hazardous material.

Safety shower/eyewash stations are tested by Facilities Management on a monthly basis. Any units which do not have a testing date within one month should be reported immediately to EH&S. If an eyewash or safety shower needs repair, call Facilities Management Trouble Call at your campus and give the operator the specific location of the defective equipment. Facilities Services Requests (FSRs) that have been generated as a result of a health and safety deficiency, such as this, must be flagged as "URGENT". A system has been implemented to expedite these FSRs.

Fire Doors

Many areas of research buildings may contain critical fire doors as part of the building design. These doors are an important element of the fire containment system and should remain closed unless they are on a magnetic self-closing or other automated self-closing system.

Safe Laboratory Habits

As detailed above, a safety program must include layers of policies and protective equipment to allow for a safe working environment, but to achieve effectiveness, a number of fundamental elements must become basic working habits for the research community. Some of these elements are detailed below:

Personal Protective Equipment:

- Wear closed-toe shoes and full length pants, or equivalent as determined by the Laboratory PPE Assessment, at all times when in the laboratory
- Utilize appropriate PPE while in the laboratory and while performing procedures that involve the use of hazardous chemicals or materials
- Confine long hair and loose clothing
- Remove laboratory coats or gloves immediately on significant contamination, as well as before leaving the laboratory

- Avoid use of contact lenses in the laboratory unless necessary. If they are used, inform supervisor so special precautions can be taken
- Use any other protective and emergency apparel and equipment as appropriate. Be aware of the locations of first aid kits and emergency eyewash and shower station

Chemical Handling:

- Properly label and store all chemicals. Use secondary containment at all times
- Deposit chemical waste in appropriately labeled receptacles and follow all other waste disposal procedures of the Chemical Hygiene Plan
- Do not smell or taste chemicals
- Never use mouth suction for pipetting or starting a siphon
- Do not dispose of any hazardous chemicals through the sewer system
- Be prepared for an accident or spill and refer to the emergency response procedures for the specific material. Procedures should be readily available to all personnel. Information on minor chemical spill mitigation may also be referenced in *Appendix M*. For general guidance, the following situations should be addressed:
 - <u>Eye Contact</u>: Promptly flush eyes with water for a prolonged period (15 minutes) and seek medical attention
 - <u>Skin Contact</u>: Promptly flush the affected area with water and remove any contaminated clothing. If symptoms persist after washing, seek medical attention

Equipment Storage and Handling:

- Store laboratory glassware with care to avoid damage. Use extra care with Dewar flasks and other evacuated glass apparatus; shield or wrap them to contain chemicals and fragments should implosion occur
- Use certified fume hoods, glove boxes, or other ventilation devices for operations which might result in release of toxic chemical vapors or dust. Preventing the escape of these types of materials into the working atmosphere is one of the best ways to prevent exposure
- Keep hood closed when you are not working in the hood
- Do not use damaged glassware or other equipment
- Do not use uncertified fume hoods or glove boxes for hazardous chemical handling
- Avoid storing materials in hoods
- Do not allow the vents or air flow to be blocked

Laboratory Operations:

- Keep the work area clean and uncluttered
- Seek information and advice about hazards, plan appropriate protective procedures, and plan positioning of equipment before beginning any new operation
- If unattended operations are unavoidable, and have been approved by the PI/Laboratory Supervisor, place an appropriate sign on the door, leave lights on, and provide for containment of toxic substances in the event of failure of a utility service (such as cooling water)
- Be alert to unsafe conditions and ensure that they are corrected when detected
- Research staff and students should never work alone on procedures involving hazardous chemicals, biological agents, or other physical hazards

• Do not engage in distracting behavior such as practical jokes in the laboratory. This type of conduct may confuse, startle, or distract another worker

Food/Drink:

- Do not eat, drink, smoke, chew gum, or apply cosmetics in areas where laboratory chemicals are present; wash hands before conducting these activities
- Do not store, handle, or consume food or beverages in storage areas, refrigerators, glassware or utensils which are also used for laboratory operations
- Wash areas of exposed skin well before leaving the laboratory

Chapter 5: Chemical Exposure Assessment

Regulatory Overview

It is UC policy to comply with all applicable health, safety and environmental protection laws, regulations and requirements. Cal/OSHA requires that all employers *"measure an employee's exposure to any substance regulated by a standard which requires monitoring if there is reason to believe that exposure levels for that substance exceed the action level (or in the absence of an action level, the exposure limit)."* Repeated monitoring may be required if initial monitoring identifies employee exposure over the action level or exposure limit.

Cal/OSHA regulates Permissible Exposure Limits (PELs) for airborne contaminants to which "*nearly all workers may be exposed daily during a 40-hour workweek for a working lifetime (of 40 years) without adverse effect*", and are based upon an 8-hour Time-Weighted Average (TWA) exposure. Thus, the PELs are the maximum permitted 8-hour TWA concentration of an airborne contaminant without the use of respiratory protection. Cal/OSHA has also defined Short Term Exposure Limits (STELs) as the maximum TWA exposure during any 15 minute period, provided the daily PEL is not exceeded and Ceiling (C) exposures that shall not be exceeded at any time.

Cal/OSHA has listed established PELs, STELs and Ceiling exposures for chemical contaminants identified in CCR Title 8 Section 5155 (Airborne Contaminants) Table AC-1 (http://www.dir.ca.gov/Title8/ac1.pdf). In the absence of a published Ceiling limit, Cal/OSHA requires employee exposure to concentrations above the PEL be controlled to prevent harmful effects. Further, Cal/OSHA has promulgated specific standards covering several regulated carcinogens, which may include an Action Level (AL), triggering medical surveillance requirements or the imposition of a specific Excursion Limit (such as for asbestos) with a unique measurement of the duration of an exposure.

Additionally, the Safe Drinking Water and Toxic Enforcement Act of 1986 requires Cal/EPA to publish annually a list of Proposition 65 chemicals known to the State to cause cancer or other reproductive toxicity (*http://www.oehha.ca.gov/prop65/prop65_list/files/P65single061110.pdf*).

Exposure Assessment Overview

All UC employees require protection from exposure to hazardous chemicals above PELs, STELs and Ceiling concentrations. Cal/OSHA requires the person supervising, directing or evaluating the exposure assessment monitoring be competent in the practice of industrial hygiene. Thus, exposure assessment should be performed only by representatives of EH&S and not the PI/Laboratory Supervisor. General questions regarding exposure assessment or the Industrial Hygiene Program can be directed to EH&S, 4-6200.

Minimizing an exposure may be accomplished using a combination of engineering controls, administrative controls and personal protective equipment, listed in order of priority. Assessing exposure to hazardous chemicals may be accomplished through a number of methods performed by EH&S, including employee interviews, visual observation of chemical use, evaluation of engineering controls, use of direct reading instrumentation, or the collection of analytical samples from the employee's breathing zone. Personal exposure assessment will be performed under either of the following situations:

- Based on chemical inventories, review of Standard Operating Procedures (SOPs), types of engineering controls present, laboratory inspection results and/or review of the annual Laboratory PPE Hazard Assessment Tool, EH&S determines whether an exposure assessment is warranted; or
- 2. User of a hazardous chemical has concern or reason to believe exposure is not minimized or eliminated through use of engineering controls or administrative practices (such as transfer of chemical through double needle performed entirely in a fume hood) and the potential for exposure exists. The user should then inform his or her Pl/Laboratory Supervisor, who will in turn contact the EH&S Industrial Hygiene Program, EH&S Radiation Safety Division, or EH&S Injury Prevention Division. EH&S will then determine the best course of action in assessing employee exposure, including visual assessment, air monitoring, medical evaluation, examination, or medical surveillance.

In event of any serious injury or exposure, including chemical splash involving dermal or eye contact, immediately call **911** from a campus phone or cell phone and obtain medical treatment immediately. Do not wait for an exposure assessment to be performed before seeking medical care.

EXPOSURE ASSESSMENT PROTOCOL – NOTIFICATION TO EMPLOYEES OR EMPLOYEE REPRESENTATIVES AND RIGHT TO OBSERVE MONITORING (SECTION 340.1)

The EH&S Industrial Hygiene Program conducts exposure assessments for members of the campus community. Employees have a right to observe testing, sampling, monitoring or measuring of employee exposure. They are also allowed access to the records and reports related to the exposure assessment. Exposure assessments may be performed for hazardous chemicals, as well as for physical hazards including noise and heat stress to determine if exposures are within PELs or other appropriate exposure limits that are considered safe for routine occupational exposure. General protocol in conducting an exposure assessment may include any of the following:

- 1. Employee interviews;
- 2. Visual observation of chemical usage and/or laboratory operations;
- 3. Evaluation of simultaneous exposure to multiple chemicals;
- 4. Evaluation of potential for absorption through the skin, mucus membranes or eyes;
- 5. Evaluating existing engineering controls (such as measuring face velocity of a fume hood);
- 6. Use of direct reading instrumentation; and
- 7. Collection of analytical samples of concentrations of hazardous chemicals taken from the employees breathing zone, or noise dosimetry collected from an employee's shirt collar or various forms of radiation dosimetry.

If exposure monitoring determines an employee exposure to be over the action level (or the PEL) for a hazard for which OSHA has developed a specific standard (e.g., lead), the medical surveillance provisions of that standard shall be followed. It is the responsibility of the PI/Laboratory Supervisor to ensure that any necessary medical surveillance requirements are met. When necessary, EH&S will make recommendations regarding adjustments engineering controls or administrative procedures to maintain exposure below any applicable PEL. Where the use of respirators is necessary to maintain exposure below permissible exposure limits, UC will provide, at no cost to the employee, the proper respiratory equipment and training. Respirators will be selected and used in accordance with the requirements of CCR Title 8 Section 5144 (*http://www.dir.ca.gov/Title8/5144.html*) and the University's Respiratory Protection Program.

In assessing exposure to hazardous chemicals for which Cal/OSHA has not published a PEL, STEL or Ceiling exposure, EH&S defers to the Threshold Limit Values (TLVs) established by the American Conference of Governmental Industrial Hygienists (ACGIH) or the Recommended Exposure Limits (RELs) established by the National Institute of Occupational Safety & Health (NIOSH). Please contact EH&S, 4-6200 for more information regarding these chemicals.

NOTIFICATION

The Industrial Hygiene Program will promptly notify the employee and his/her PI/Laboratory Supervisor of the results in writing (within 15 working days or less if required) after the receipt of any monitoring results. The Industrial Hygiene Program will establish and maintain an accurate record of any measurements taken to monitor exposures for each employee. Records, including monitoring provided by qualified vendors, will be managed in accordance with CCR Title 8 Section 3204 "Access to Employee Exposure and Medical Records" (*http://www.dir.ca.gov/Title8/3204.html*).

EXPOSURE ASSESSMENT USE TO DETERMINE AND IMPLEMENT CONTROLS

EH&S will use any of the following criteria to determine required control measures to reduce employee's occupational exposure:

- 1. Verbal information obtained from employees regarding chemical usage;
- 2. Visual observations of chemical use or laboratory operations;
- 3. Evaluation of existing engineering control measures or administrative practices;
- 4. Recommendations expressed in Safety Data Sheets;
- 5. Regulatory requirements of Cal/OSHA;
- 6. Recommendations from professional industrial hygiene organizations;
- 7. Direct reading instrumentation results;
- 8. Employee exposure monitoring results; and/or
- 9. Medical evaluation, examination and/or surveillance findings.

Particular attention shall be given to the selection of safety control measures for chemicals that are known to be extremely hazardous. Per Cal/OSHA CCR Title 8 Section 5141 "Control of Harmful Exposure to Employees" (*http://www.dir.ca.gov/Title8/5141.html*), the control of harmful exposures shall be prevented by implementation of control measures in the following order:

- 1. Engineering controls, whenever feasible;
- 2. Administrative controls whenever engineering controls are not feasible or do not achieve full compliance and administrative controls are practical; and
- 3. Personal protective equipment, including respiratory protection, during:
 - a. the time period necessary to install or implement feasible engineering controls
 - b. when engineering and administrative controls fail to achieve full compliance
 - c. in emergencies.

Medical Evaluation

All employees, student workers, medical health services volunteers, or laboratory personnel who work with hazardous chemicals shall have an opportunity to receive a free medical evaluation, including supplemental examinations which the evaluating physician determines necessary, under the following circumstances:

- 1. Whenever an employee develops signs or symptoms associated with a hazardous chemical to which an employee may have been exposed in a laboratory;
- 2. Where personal monitoring indicates exposure to a hazardous chemical is above a Cal/OSHA Action Level (AL) or Permissible Exposure Limit (PEL) or recommended exposure levels established by the National Institute for Occupational Safety & Health (NIOSH) or the American Conference of Governmental Industrial Hygienists (ACGIH) in the event Cal/OSHA has not established an AL or PEL for a particular hazardous chemical;
- 3. Whenever an uncontrolled event takes place in the work area such as a spill, leak, explosion, fire, etc., resulting in the likelihood of exposure to a hazardous chemical; or
- 4. Upon reasonable request of the employee to discuss medical issues and health concerns regarding work-related exposure to hazardous chemicals.

All work-related medical evaluations and examinations will be performed by licensed physicians or staff under the direct supervision of a licensed physician. Evaluations and examinations will be provided without cost to the employee, without loss of pay, and at a reasonable time and place.

Any laboratory employee or student worker who exhibits signs and symptoms of adverse health effects from work-related exposure to a hazardous chemical should report immediately for a medical evaluation.

Refer to UC's Injury & Illness Prevention Program (IIPP) for procedures on how to obtain medical evaluation under the above-listed circumstances. The UCI IIPP Program is on the EH&S website at http://www.ehs.uci.edu/programs/iipp/hsprog.html

Information to Provide to the Clinician

At the time of the medical evaluation, the following information shall be provided to the examining physician:

- 1. Personal information such as age, weight and campus employee ID number;
- 2. Common and/or IUPAC name of the hazardous chemicals to which the individual may have been exposed;
- 3. A description of the conditions under which the exposure occurred;
- 4. Quantitative exposure data, if available;
- 5. A description of the signs and symptoms of exposure that the employee is experiencing, if any;
- 6. A copy of the Safety Data Sheet (SDS) of the hazardous chemical in question;
- 7. History of exposure including previous employment and non-occupational (recreational) hobbies; and
- 8. Any additional information helpful in assessing or treating an exposure or injury such as a biological component of exposure or existence of an antitoxin.



Physician's Written Opinion

For evaluation or examinations required by Cal/OSHA, the employer shall receive a written opinion from the examining physician which shall include the following:

- 1. Recommendation for further medical follow-up;
- 2. Results of the medical examination and any associated tests, if requested by the employee;
- 3. Any medical condition which may be revealed in the course of the examination which may place the employee at increased risk as a result of exposure to a hazardous chemical found in the workplace; and
- 4. A statement that the employee has been informed by the physician of the results of the consultation or medical examination and any medical condition that may require further examination or treatment.

Confidentiality & Individual's Access to Personal Medical Records

All patient medical information is protected by California and federal law and is considered strictly confidential. The examining physician is prohibited from disclosing any patient medical information that is not directly related to the work-related exposure under evaluation and should not reveal any diagnosis unrelated to exposure. Any patient information disclosed by The examining physician to the employee's supervisor will be limited to information necessary in assessing an employee's return to work, including recommended restrictions in work activities, if any. Any patient information disclosed by the examining physician to EH&S will be limited to information necessary to develop a course of exposure monitoring, or perform hazard assessments and incident investigations, if appropriate. The examining physician will otherwise disclose patient medical information only as required by California and Federal law, such as for Worker's Compensation Insurance claims. Each employee has the right to access his/her own personal medical and exposure records. The examining physician will provide an employee with a copy of his/her medical records upon written request.

Medical Surveillance

Medical surveillance is the process of using medical examinations, questionnaires and/or biological monitoring to determine potential changes in health as a result of exposure to a hazardous chemical or other hazards. Certain Cal/OSHA standards require clinical examination as part of medical surveillance when exposure monitoring exceeds an established Action Level or PEL.

Outside vendors may provide medical surveillance services. Medical surveillance is required of employees who are routinely exposed to certain hazards as part of their job description (such as asbestos) and may be offered to other employees based upon guantifiable or measured exposure. Examples of hazards that are monitored through the medical surveillance program may include:

• Asbestos

Noise (Hearing Conservation Program)

- Beryllium
- Formaldehyde
- Lead
- Methylene Chloride

- Radioactive Chemicals (Bioassay Program)
- Respirator Use (Respirator Protection Program)
- Other Particularly Hazardous Substances

Individuals with questions regarding work-related medical surveillance are encouraged to contact EH&S for more information.

Chapter 6: Inventory, Labeling, Storage, and Transport

Chemical Inventories

Each laboratory group is required to maintain a current chemical inventory that lists the chemicals and compressed gases used and stored in the labs and the quantity of these chemicals. Specific storage locations must be kept as part of the inventory list to ensure that they can be easily located. Chemical inventories are used to ensure compliance with storage limits and fire regulations and can be used in an emergency to identify potential hazards for emergency response operations.

The chemical inventory list should be reviewed prior to ordering new chemicals and only the minimum quantities of chemicals necessary for the research should be purchased. As new chemicals are added to the inventory, each laboratory group must confirm that they have access to the Safety Data Sheet (SDS) for that chemical. Where practical, each chemical should be dated so that expired chemicals can be easily identified for disposal. Inventory the materials in your laboratory frequently (at least annually) to avoid overcrowding with materials that are no longer useful and note the items that should be replaced, have deteriorated, or show container deterioration. Unneeded items should be returned to the storeroom/stockroom and compromised items should be discarded as chemical waste.

Indications for disposal include:

- Cloudiness in liquids
- Color change
- Evidence of liquids in solids, or solids in liquids
- "Puddling" of material around outside of containers
- Pressure build-up within containers
- Obvious deterioration of containers

Access to hazardous chemicals, including toxic and corrosive substances, should be restricted at all times. These materials must be stored in laboratories or storerooms that are kept locked when laboratory personnel are not present. Locked storage cabinets or other precautions are always recommended, and in some cases may be required in the case of unusually toxic or hazardous chemicals. Unusually toxic chemicals may include those that are associated with very low immediately dangerous to life or health (IDLH) conditions. For guidance on locked storage requirements, please contact EH&S, 4-6200.

On termination or transfer of laboratory personnel, all related hazardous materials should be properly disposed of, or transferred to the laboratory supervisor or a designee.

Chemical Labeling

Every chemical found in the laboratory must be properly labeled. Most chemicals come with a manufacturer's label that contains the necessary information, so care should be taken to not damage

or remove these labels. Each chemical bottle, including diluted chemical solutions, must be labeled with its contents and the hazards associated with this chemical. It is recommended that each bottle also be dated when received and when opened to assist in determining which chemicals are expired and require disposal. When new chemicals and compounds are generated by laboratory operations, these new chemical bottles must be labeled with the name, date, and hazard information; the generator or other party responsible for this chemical should be named on the container so that they may be contacted if questions arise about the container's contents. Printable safety labels are available at http://www.ehs.uci.edu/programs/enviro/.

Peroxide forming chemicals (e.g., ethers) (*Appendix H*) must be labeled with a date on receipt and on first opening the bottle. These chemicals are only allowed a one year shelf life and should be disposed of as waste in one year. These chemicals can degrade to form shock sensitive, highly reactive compounds and should be stored and labeled very carefully.

Particularly Hazardous Substances (see *Chapter 3*) require additional labeling to identify the specific hazard associated with each of these chemicals (carcinogen, reproductive toxin, acute toxin). In addition, the storage area where they are kept must be labeled with the type of hazard. These chemicals should be segregated from less hazardous chemicals to help with proper access control and hazard identification.

Chemical Storage & Segregation

Establish and follow safe chemical storage & segregation procedures for your laboratory.

Storage guidelines are included for materials that are flammable, oxidizers, corrosive, water reactive, explosive and highly toxic. The specific Safety Data Sheet (SDS) should always be consulted when doubts arise concerning chemical properties and associated hazards. All procedures employed must comply with Cal/OSHA, Fire Code and building code regulations. Always wear appropriate personal protective equipment (e.g., laboratory coat, safety glasses, gloves, safety goggles, apron) when handling hazardous chemicals. Be aware of the locations of the safety showers and emergency eyewash stations. Each laboratory is required to provide appropriate laboratory-specific training on how to use this equipment **prior** to working with hazardous chemicals. Table 6.1 lists chemical safety storage priorities.

Table 6.1 – Chemical Safety Storage Priorities

Keep in mind that most chemicals have multiple hazards and a decision must be made as to which storage area would be most appropriate for each specific chemical. First you have to determine your priorities:

- 1. **Flammability.** When establishing a storage scheme, the number one consideration should be the flammability characteristics of the material. If the material is flammable, it should be stored in a flammable cabinet.
- 2. **Isolate.** If the material will contribute significantly to a fire (e.g., oxidizers), it should be isolated from the flammables. If there were a fire in the laboratory and response to the fire with water would exaggerate the situation, isolate the water reactive material away from contact with water.
- 3. **Corrosivity.** Next look at the corrosivity of the material, and store accordingly.
- 4. **Toxicity.** Finally, consider the toxicity of the material, with particular attention paid to regulated materials. In some cases, this may mean that certain chemicals will be isolated within a storage area. For example, a material that is an extreme poison but is also flammable, should be locked away in the flammable storage cabinet to protect it against accidental release.

There will always be some chemicals that will not fit neatly in one category or another, but with careful consideration of the hazards involved, most of these cases can be handled in a reasonable fashion.

GENERAL RECOMMENDATIONS FOR SAFE STORAGE OF CHEMICALS

Each chemical in the laboratory must be stored in a specific location and returned there after each use. Acceptable chemical storage locations may include corrosive cabinets, flammable cabinets, laboratory shelves, or appropriate refrigerators or freezers. Fume hoods should not be used as general storage areas for chemicals, as this may seriously impair the ventilating

capacity of the hood. Figure 6.2 depicts improper fume hood storage. Chemicals should not be routinely stored on bench tops or stored on the floor. Additionally, bulk quantities of chemicals (i.e., larger than one-gallon) should be stored in a separate storage area, such as a stockroom or supply room.

Laboratory shelves should have a raised lip along the outer edge to prevent containers from falling. Hazardous liquids or corrosive chemicals should not be stored on shelves above eye-level and chemicals which are highly toxic or corrosive should be in unbreakable secondary containers. Figure 6.2 – Improper Fume Hood Storage



Chemicals must be stored at an appropriate temperature and humidity level and should **never** be stored in direct sunlight or near heat sources, such as laboratory ovens. Incompatible materials should be stored in separate cabinets, whenever possible. If these chemicals must be stored in one cabinet, due to space limitations, adequate segregation and secondary containment must be ensured to prevent adverse reactions. All stored containers and research samples must be appropriately labeled and tightly capped to prevent vapor interactions and to alleviate nuisance odors. Flasks with cork, rubber or glass stoppers should be avoided because of the potential for leaking.

Laboratory refrigerators and freezers must be labeled appropriately with "No Food/Drink" and must **never** be used for the storage of consumables. Freezers should be defrosted periodically so that chemicals do not become trapped in ice formations. **Never** store peroxide formers (e.g., ether) in a refrigerator!

FLAMMABLE AND COMBUSTIBLE LIQUIDS

Large quantities of flammable or combustible materials should not be stored in the laboratory. The maximum total quantity of flammable and combustible liquids must not exceed **60 gallons** within a flammable storage cabinet. The maximum quantity allowed to be kept outside a flammable storage cabinet, safety can, or approved refrigerator/freezer is **10 gallons**. Only the amounts needed for the current procedure should be kept on bench tops and the remainder should be kept in flammable storage cabinets, explosion proof refrigerators/freezers that are approved for the storage of flammable substances, or approved safety cans or drums that are grounded. Always segregate flammable or combustible liquids from oxidizing acids and oxidizers. Flammable materials must **never** be stored in domestic-type refrigerators/freezers and should not be stored in a refrigerator/freezer if the chemical has a flash point below the temperature of the equipment. Flammable or combustible liquids must not be stored on the floor or in any exit access.

Handle flammable and combustible substances only in areas free of ignition sources and use the chemical in a fume hood whenever practical. Only the amount of material required for the experiment or procedure should be stored in the work area. Always transfer flammable and combustible chemicals from glass containers to glassware or from glass container/glassware to plastic. Transferring these types of chemicals between plastic containers may lead to a fire hazard due to static electricity. The transfer of flammable liquid from 5 gallon or larger metal containers should **not** be done in the laboratory.

PYROPHORIC & WATER REACTIVE SUBSTANCES

Because pyrophoric substances can spontaneously ignite on contact with air and/or water, they must be handled under an inert atmosphere and in such a way that rigorously excludes air and moisture. Some pyrophoric materials are also toxic and many are dissolved or immersed in a flammable solvent. Other common hazards include corrosivity, teratogenicity, or peroxide formation.

Only minimal amounts of reactive chemicals should be used in experiments or stored in the laboratory. These chemicals must be stored as recommended in the SDS. Reactive materials containers must be clearly labeled with the correct chemical name, in English, along with a hazard warning.

Suitable storage locations may include inert gas-filled desiccators or glove boxes; however, some pyrophoric materials must be stored in a flammable substance approved freezer. If pyrophoric or water reactive reagents are received in a specially designed shipping, storage or dispensing container (such as the Aldrich Sure/Seal packaging system), ensure that the integrity of that container is maintained. Ensure that sufficient protective solvent, oil, kerosene, or inert gas remains in the container while pyrophoric materials are stored. Never store reactive chemicals with flammable materials or in a flammable liquids storage cabinet.

Storage of pyrophoric gases is described in the California Fire Code, Chapter 41. Gas cabinets, with remote sensors and fire suppression equipment, are required. Gas flow, purge and exhaust systems should have redundant controls to prevent pyrophoric gas from igniting or

exploding. Emergency back-up power should be provided for all electrical controls, alarms and safeguards associated with the pyrophoric gas storage and process systems.

Never return excess reactive chemical to the original container. Small amounts of impurities introduced into the container may cause a fire or explosion. For storage of excess chemical, prepare a storage vessel in the following manner:

- 1. Dry any new empty containers thoroughly;
- 2. Insert the septum into the neck in a way that prevents atmosphere from entering the clean dry (or reagent filled) flask;
- 3. Insert a needle to vent the flask and quickly inject inert gas through a second needle to maintain a blanket of dry inert gas above the reagent;
- 4. Once the vessel is fully purged with inert gas, remove the vent needle then the gas line. To introduce the excess chemical, use the procedure described in the handling section, below;
- 5. For long-term storage, the septum should be secured with a copper wire;
- 6. For extra protection a second same-sized septa (sans holes) can be placed over the first; and
- 7. Use parafilm around the outer septa and remove the parafilm and outer septum before accessing the reagent through the primary septum.

The EH&S *Pyrophoric Reagent SOP (Appendix I) and Safety* video provide information about the safe handling of pyrophoric chemicals and can be viewed online at: <u>Pyrophoric Reagent</u> (SOP) and <u>Pyrophoric Safety</u> (Video).

OXIDIZERS

Oxidizers (e.g., hydrogen peroxide, ferric chloride, potassium dichromate, sodium nitrate) should be stored in a cool, dry place and kept away from flammable and combustible materials, such as wood, paper, Styrofoam, plastics, flammable organic chemicals, and away from reducing agents, such as zinc, alkaline metals, and formic acid.

PEROXIDE FORMING CHEMICALS

Peroxide forming chemicals (e.g., ethyl ether, diethylether, cyclohexene) should be stored in airtight containers in a dark, cool, and dry place and must be segregated from other classes of chemicals that could create a serious hazard to life or property should an accident occur (e.g., acids, bases, oxidizers). The containers should be labeled with the date received and the date opened. This information, along with the chemical identity should face forward to minimize container handling during inspection. These chemicals must also be tested and documented for the presence of peroxides periodically. Minimize the quantity of peroxide forming chemicals stored in the laboratory and dispose of peroxide forming chemicals before peroxide formation. Refer to Appendix H for specific guidelines and/or contact EH&S, 4-6200 with questions.

Carefully review all cautionary material supplied by the manufacturer prior to use. Avoid evaporation or distillation, as distillation defeats the stabilizer added to the solvents. Ensure that containers are tightly sealed to avoid evaporation and that they are free of exterior contamination or crystallization. **Never** return unused quantities back to the original container and clean all spills immediately.

If old containers of peroxide forming chemicals are discovered in the laboratory, (greater than two years past the expiration date or if the date of the container is unknown), **do not handle the**

container. If crystallization is present in or on the exterior of a container, **do not handle the container**. Secure it and contact EH&S, 4-6200 for pick-up and disposal.

CORROSIVES

Store corrosive chemicals (i.e., acids, bases) below eye level and in secondary containers that are large enough to contain at least 10% of the total volume of liquid stored or the volume of the largest container, whichever is greater. Acids must always be segregated from bases and from active metals (e.g., sodium, potassium, magnesium) at all times and must also be segregated from chemicals which could generate toxic gases upon contact (e.g., sodium cyanide, iron sulfide).

Specific types of acids require additional segregation. Mineral acids must be kept away from organic acids and oxidizing acids must be segregated from flammable and combustible substances. Perchloric acid should be stored by itself, away from other chemicals. Picric Acid is reactive with metals or metal salts and explosive when dry and must contain at least 10% water to inhibit explosion.

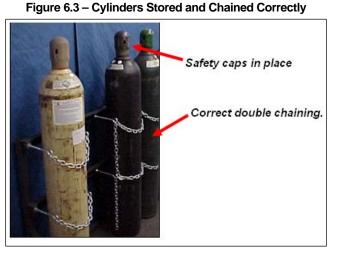
SPECIAL STORAGE REQUIREMENTS

Compressed Gas Cylinders

Compressed gas cylinders that are stored in the laboratory must be chained to the wall, with the safety cap in place. The cylinders must be restrained by two chains; one chain must be placed at one third from the top of the cylinder, and the other placed at one third from the bottom of the cylinder (see Figure 6.3). Bolted "clam shells" may be used in instances where gas cylinders must be stored or used away from the wall. Store liquefied fuel-gas cylinders securely in the upright position. **Cylinders containing certain gases are prohibited from being stored in a horizontal position, including those which contain a water volume of more than 5 liters.** Do not expose cylinders to excessive dampness, corrosive chemicals or fumes.

Certain gas cylinders require additional precautions. Flammable gas cylinders must use only flame-resistant gas lines and hoses which carry flammable or toxic gases from cylinders and must have all connections wired. Compressed oxygen gas cylinders must be stored at least 20 feet away from combustible materials and flammable gases.

Gas cylinder connections must be inspected frequently for deterioration and must never be used without a regulator. Never use a leaking, corroded or damaged cylinder and never refill compressed gas cylinders. When stopping a leak between cylinder and



regulator, always close the valve before tightening the union nut. The regulator should be replaced with a safety cap when the cylinder is not in use. Move gas cylinders with the safety cap in place using carts designed for this purpose. Refer to the UCI Compressed Gases Safety Program (http://www.ehs.uci.edu/programs/safety/compressgasprog.html) for further details.

Liquid Nitrogen

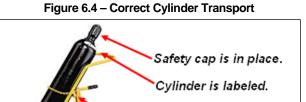
Because liquid nitrogen containers are at low pressure and have protective rings mounted around the regulator, they are not required to be affixed to a permanent fixture such as a wall. However, additional protection considerations should be addressed when storing liquid nitrogen in a laboratory. The primary risk to laboratory personnel from liquid nitrogen is skin or eye thermal damage caused by contact with the material. In addition, nitrogen expands 696:1 when changing from a cryogenic liquid to a room temperature gas. The gases usually are not toxic, but if too much oxygen is displaced, asphyxiation is a possibility. Always use appropriate thermally insulated gloves when handling liquid nitrogen. Face shields may be needed in cases where splashing can occur.

On-Campus Distribution of Hazardous Chemicals

Precautions must be taken when transporting hazardous substances between laboratories. Chemicals must be transported between stockrooms and laboratories in break-resistant, secondary containers such as commercially available bottle carriers made of rubber, metal, or plastic, that include carrying handle(s) and which are large enough to hold the contents of the chemical container in the event of breakage.

When transporting cylinders of compressed gases, always secure the cylinder with straps or chains onto a suitable hand truck and protect the valve with a cover cap. Avoid dragging, sliding, or rolling cylinders and use a freight elevator when possible. Figure 6.4 illustrates correct cylinder transport.

Off-Campus Distribution of Hazardous Chemicals



Cylinder is chained to dolly.

The transportation of hazardous chemicals and compressed gases over public roads, or by air, is strictly governed by international, federal, and state regulatory agencies, including the U.S. Department of Transportation (DOT) and the International Air Transport Association (IATA). Any person who prepares and/or ships these types of materials must ensure compliance with pertinent regulations regarding training, quantity, packaging, and labeling. Without proper training, it is illegal to ship hazardous materials. Those who violate the hazardous materials shipment regulations are subject to criminal investigation and penalties. UC campus personnel who sign hazardous materials manifests, shipping papers, or those who package hazardous material for shipment, must be trained and certified by EH&S.

Individuals who wish to ship or transport hazardous chemicals or compressed gases off-campus, even when using UC or personal vehicles, must contact EH&S, 4-6200 for assistance.

For more information regarding hazardous material shipping responsibilities, training requirements and FAQs, refer to http://www.ehs.uci.edu/programs/dgoods/index.html

Chapter 7: Training

Introduction

Effective training is critical to facilitate a safe and healthy work environment and prevent laboratory accidents. All PIs/Laboratory Supervisors must participate in formal safety training and ensure that all their employees have appropriate safety training before working in a laboratory. EH&S provides both classroom and online training to help meet this requirement on the UC Learning Center website at http://www.uclc.uci.edu/

Types of Training

All laboratory personnel must complete general safety training before:

- 1. Beginning work in the laboratory;
- 2. Prior to new exposure situations; and
- 3. As work conditions change.

Refresher training is also required for all laboratory personnel. EH&S offers general classroom and online training, plus resource materials to assist laboratories in implementing laboratory-specific training.

GENERAL LABORATORY SAFETY TRAINING

Anyone working in a laboratory is required to complete laboratory safety training, which includes:

- Review of laboratory rules and regulations, including the Chemical Hygiene Plan
- Recognition of laboratory hazards
- Use of engineering controls, administrative controls and personal protective equipment to mitigate hazards
- Exposure limits for hazardous chemicals
- Signs and symptoms associated with exposures to hazardous chemicals
- Chemical exposure monitoring
- Review of reference materials (e.g., SDS) on hazards, handling, storage and disposal of hazardous chemicals
- Procedures for disposing of hazardous chemical waste
- Fire safety and emergency procedures
- Information required by Section 3204 regarding access to employee exposure and medical records (annually required)

All employees must take one of the following basic laboratory safety classes provided by EH&S as appropriate for their employment status:

- Laboratory Core Safety for anyone working in a laboratory
- **Principal Investigators Creating a Safety Culture** for PIs responsible for implementing a laboratory safety plan

• Laboratory Supervisors Creating a Safety Culture – for Laboratory Supervisors responsible for implementing a laboratory safety plan

General safety training requirements are determined by completing the Safety Training Self-Assessment described at http://www.ehs.uci.edu/SafetyTrainingSelf-AssessmentInstructions.pdf. Log into the UC Learning Center to complete your self-assessment at http://www.uclc.uci.edu/

LABORATORY-SPECIFIC TRAINING

Pls/Laboratory Supervisors must also provide laboratory-specific training. Topics that require specific training include:

- Location and use of the Chemical Hygiene Plan, IIPP, SDS(s) and other regulatory information
- Review of IIPP and Emergency Management Plan, including location of emergency equipment and exit routes
- Specialized equipment
- Standard Operating Procedures
- Specialized procedures and protocols
- Particularly Hazardous Substances including physical and health hazards, potential exposure, medical surveillance, and emergency procedures

Resources

EH&S has a number of tools available for laboratories to simplify the completion of appropriate training, including:

- Online training modules (http://www.uclc.uci.edu/)
 - Bloodborne Pathogens
 - Chemical Fume Hood
 - Fire Extinguisher Safety
 - Formaldehyde Safety
 - Hazard Communication
 - o Hazardous Waste
 - o Laboratory Core Safety
 - Laboratory Supervisors Creating a Safety Culture
 - Principal Investigators Creating a Safety Culture
 - Standard Operating Procedures (http://www.ehs.uci.edu/programs/sop_library/index.html)
 - Hazardous Operations SOPs
 - Hazardous Material Class SOPs (control banded chemicals)
 - Hazardous Material SOPs
 - Pyrophoric Reagent (SOP) and Pyrophoric Safety (Video)
 - UC Center for Lab Safety SOP Library
- Fact Sheets (http://www.ehs.uci.edu/programs/sop_library/index.html)
 - Anesthetic Gases (Fact Sheet)
 - o Azide (Fact Sheet)
 - o Hazardous Chemical Categories General Lab (Fact Sheet)
 - Hazardous Chemical Categories INRF (Fact Sheet)

- DVD Lending Library (<u>http://www.ehs.uci.edu/train.html</u>)
 - Chemical Hygiene/Laboratory Safety
 - Hazard Communication and General Safety
 - Respiratory Protection
 - Waste Management

EH&S provides additional assistance in planning laboratory-specific training upon request.

Documentation of Training

Accurate recordkeeping is a critical component of health and safety training. Per OSHA regulations, departments or laboratories are responsible for documenting health and safety training, including safety meetings, one-on-one training, and classroom and online training. Documentation should be maintained in the Safety On Site Binder. Additional information on recordkeeping can be found in *Chapter 8: Compliance and Enforcement.*

The UC Learning Center website (http://www.uclc.uci.edu/) documents training history for all courses completed online.

EH&S provides recordkeeping resources. See the EH&S website (http://www.ehs.uci.edu/) for a Work- Unit Specific Training Roster template at http://www.ehs.uci.edu/programs/iipp/Work_Unit-Specific_Training_Roster.doc.(*Appendix J*).

Chapter 8: Inspections and Compliance

Laboratory Safety Inspections

EH&S has a comprehensive laboratory safety compliance program to assist laboratories and other facilities that use, handle or store hazardous chemicals to maintain a safe work environment. This program helps to ensure compliance with regulations and to fulfill UC's commitment to protecting the health and safety of the campus community.

As part of this laboratory safety program, EH&S conducts periodic inspections of laboratories and other facilities with hazardous chemicals to ensure the laboratory is operating in a safe manner and to ensure compliance with all federal, state and university safety requirements. The primary goal of inspection is to identify both existing and potential accident-causing hazards, actions, faulty operations and procedures that can be corrected **before** an accident occurs. UCI policy

(http://www.ehs.uci.edu/programs/gensafe/HazardReportingCorrectionRedTagProcedures.doc) explicitly authorizes EH&S to order the cessation of any activity that is "Immediately Dangerous to Life and Health" (IDLH) until that hazardous condition or activity is abated.

The laboratory safety inspection is comprehensive in nature and looks into all key aspects of working with hazardous chemicals. While inspections are a snapshot in time and cannot identify every accident-causing mistake, they do provide important information on the overall operation of a particular laboratory. They can also help to identify weaknesses that may require more systematic action across a broader spectrum of laboratories, and strengths that should be fostered in other laboratories. The complete inspection checklist can be found in *Appendix K*. Specific inspection compliance categories include:

- 1. Documentation and Training;
- 2. Hazard Communication (including review of SOPs);
- 3. Emergency and Safety Information;
- 4. Fire Safety;
- 5. General Safety;
- 6. Use of personal protective equipment (PPE);
- 7. Housekeeping;
- 8. Chemical Storage;
- 9. Fume Hoods;
- 10. Chemical Waste Disposal and Transport;
- 11. Seismic Safety; and
- 12. Mechanical and Electrical Safety.

Planned, focused assessments are also conducted. Examples of these include industrial hygiene assessments and unannounced PPE inspections. Once the inspection is completed, EH&S issues a Laboratory Inspection Report via email. The report identifies deficiencies in the laboratory, both critical and non-critical. Critical deficiencies are those that have the potential to lead to serious injuries or be of critical importance in the event of an emergency. These deficiencies must be immediately corrected. Non-critical deficiencies must be corrected within 30-days. Any deficiency that requires a "Facilities Management Request" (FMR) for completion will be added to the FMR database so that it can be expedited by Facilities Management. The *Laboratory Inspection Report* format is shown in Appendix K. A copy of the most recent *Laboratory Inspection Report* should be maintained as part of the records inside the Safety On Site Binder.

NOTIFICATION AND ACCOUNTABILITY

The compliance program requires that PIs/Laboratory Supervisors and other responsible parties take appropriate and effective corrective action upon receipt of written notification of inspection findings. Critical deficiencies are required to be corrected within 48-hours; non-critical deficiencies must be corrected within 30-days. Failure to take corrective actions within the required timeframe will result in a repeat deficiency finding and an escalation of the notification to the Department Chair, Dean and Vice-Chancellor for Research. Depending on the severity of the deficiency, the EH&S Director, in consultation with the Vice-Chancellor for Research and Laboratory Safety Committee, may temporarily suspend research activities until the violation is corrected. In some cases, the PI may be required to provide a corrective action plan prior to resumption of research activities.

RECORDKEEPING REQUIREMENTS

Accurate recordkeeping demonstrates a commitment to the safety and health of the UC community, integrity of research, and protection of the environment. EH&S is responsible for maintaining records of inspections, accident investigations, equipment calibration, and training conducted by EH&S staff. Per OSHA regulations, departments or laboratories must document health and safety training, including safety meetings, one-on-one training, and classroom and online training. Additionally, the following records must be retained in accordance with the requirements of state and federal regulations:

- 1. Accident records;
- 2. Measurements taken to monitor employee exposures;
- 3. Chemical Hygiene Plan records should document that the facilities and precautions were compatible with current knowledge and regulations;
- 4. Inventory and usage records for high-risk substances should be kept;
- 5. Any medical consultation and examinations, including tests or written opinions required by CCR, Title 8, Section 5191; and
- 6. Medical records must be retained in accordance with the requirements of state and federal regulations.

Chapter 9: Hazardous Chemical Waste Management

Hazardous Waste Program

The EH&S Hazardous Waste Program manages the shipment and disposal of all hazardous waste generated on campus. Each laboratory employee must comply with the campus Hazardous Waste Management Program requirements (http://www.ehs.uci.edu/programs/enviro/) and all applicable

regulations. Hazardous waste pick-up service is provided to all UCI hazardous waste generators. Laboratory personnel are responsible for identifying hazardous waste, labeling it, storing it properly in the laboratory. Laboratory clean-outs and disposal of high hazard compounds must be scheduled in advance. The PI/Laboratory Supervisor is responsible for coordinating the disposal of all chemicals from his/her laboratories prior to closing down laboratory operations.



Regulation of Hazardous Waste

In California, hazardous waste is regulated by the Department of Toxic Substance Control (DTSC), a division within the California Environmental Protection Agency (Cal/EPA). Federal EPA regulations also govern certain aspects of hazardous waste management, since most of our waste is treated and disposed out of state. These hazardous waste regulations are part of the Resource Conservation and Recovery Act, or RCRA. Local enforcement authority is administered by the Orange County Health Care Agency Environmental Health Division.

DEFINITION OF HAZARDOUS WASTE

Federal and State regulations define hazardous waste as a substance that poses a hazard to human health or the environment when improperly managed. A chemical waste is considered hazardous if it is either listed on one of the lists of hazardous wastes found in the Federal or State regulations, or exhibits one or more of the four characteristics listed below.

- Ignitable
 - Flashpoint <140 degrees F
 - Capable of causing fire at standard temperature and pressure through friction, absorption of moisture, or spontaneous chemical changes
 - o Is an ignitable compressed gas
 - Is an oxidizer
- Corrosive
 - Liquid with pH less than or equal to 2 or greater than or equal to 12.5
 - Solid that has pH less than or equal to 2 or greater than or equal to 12.5 when mixed with equal weight of water
- Reactivity

- o Normally unstable and readily undergoes violent change
- Reacts violently with water
- Forms potentially explosive mixtures with water
- Forms toxic gases, vapors, or fumes when mixed with water
- Is a cyanide or sulfide bearing waste which, when exposed to pH conditions between 2 and 12.5, can generate toxic gases, vapors, or fumes
- Is capable of detonation or explosive decomposition if subjected to a strong initiating source or heated under confinement
- o Is readily capable of detonation or reaction at standard temperature and pressure
- Toxicity
 - Has an acute oral LD50 less than 2,500 mg/kg
 - Has an acute dermal LD50 less than 4,300 mg/kg
 - Has an acute inhalation LC50 less than 10,000 ppm as a gas or vapor
 - Has an acute aquatic 96-hour LC50 less than 500 mg/l
 - Has been shown through experience or testing to pose a hazard to human health or environment because of its carcinogenicity (carcinogen, mutagen, teratogen), acute toxicity, chronic toxicity, bioaccumulative properties, or persistence in the environment

Hazardous chemicals that are stored in containers that are unlabeled or mislabeled, in poor condition, or abandoned are also considered hazardous waste.

Used lubricating oil must be managed as a hazardous waste.

Engineered nanomaterials such as nanotubes, nanorods, nanowires, quantum dots, etc. must be managed as a hazardous waste.

EXTREMELY HAZARDOUS WASTE

Certain compounds meet an additional definition known as "extremely hazardous waste". This list of compounds includes carcinogens, pesticides, and reactive compounds, among others (e.g., formaldehyde, chloroform, and hydrofluoric acid). The Federal EPA refers to this waste as "acutely hazardous waste", but Cal/EPA has published a more detailed list of extremely hazardous waste. Both the State and the Federal lists are included in the EH&S list of extremely hazardous waste, found at: http://www.ehs.uci.edu/programs/enviro/AcutelyExtremelyHazardousWaste.xls NOTE: While there is some overlap with the list of Particularly Hazardous Substances, such as the examples listed above, the extremely hazardous waste list is specific to the hazardous waste management program.

Proper Hazardous Waste Management

TRAINING

All personnel who are responsible for handling, managing or disposing of hazardous waste must attend training **prior** to working with these materials. The EH&S online Hazardous Waste training course covers the hazardous waste program requirements and includes training on container labeling (http://www.ehs.uci.edu/programs/enviro/). To complete Hazardous Waste training, log on to the UC Learning Center website at http://www.uclc.uci.edu/

WASTE IDENTIFICATION

All the chemical constituents in each hazardous waste stream must be accurately identified by knowledgeable laboratory personnel. This is a critical safety issue for both laboratory employees and the waste technicians that handle the waste once it is turned over to EH&S. Mixing of incompatible waste streams has the potential to create violent reactions and is a common cause of laboratory accidents. If there is uncertainty about the composition of a waste stream resulting from an experimental process, laboratory workers must consult the PI/Laboratory Supervisor, the Chemical Hygiene Officer or the Hazardous Waste Manager. In most cases, careful documentation and review of all chemical products used in the experimental protocol will result in accurate waste stream characterization.

The manufacturer's SDS provides detailed information on each hazardous ingredient in laboratory reagents and other chemical products, and also the chemical, physical, and toxicological properties of that ingredient. The UC SDS library (*http://www.ucmsds.com*) provides an extensive library of research chemicals.

LABELING

Hazardous waste labels must be placed on the hazardous waste container upon the start of accumulation. Labels are available online at www.ehs.uci.edu/programs/enviro/.

STORAGE

- Hazardous waste must be transferred to EH&S for disposal within 6 months of being generated.
- Hazardous waste containers must be stored in secondary containment to adequately contain all of the contents of the container.
- Hazardous waste containers must be kept closed, except when adding waste.
- Hazardous waste that meets the quantity threshold of 55 gallons of hazardous waste or 1 quart of acutely / extremely hazardous waste must be transferred to EH&S for disposal within 3 days of reaching these set volumes.
- Report damaged containers to EH&S. EH&S can provide assistance to transfer the contents of the damaged container to an appropriate container.
- Containers must be inspected weekly for signs of leaks, corrosion, or deterioration.
- Do not dispose of chemicals by pouring them down the drain or placing them in the trash.
- Do not use fume hoods to evaporate chemicals.

SEGREGATION

All hazardous waste must be segregated to prevent incompatible mixtures.

Segregation can be by hazard class. Hazard class examples include:

• Flammable, Oxidizer, Pyrophoric, Reactive, Reducer, Acid, Base, and Toxic For more information on specific chemical incompatibility, consult a safety data sheet (SDS).

INCOMPATIBLE WASTE STREAMS

Mixing incompatible waste streams, or selecting a container that is not compatible with its contents, is a common cause of accidents in laboratories and waste storage facilities. Reactive mixtures can rupture containers and explode, resulting in serious injury and property damage. All chemical constituents and their waste byproducts must be compatible for each waste container generated. Waste labels must be immediately updated when a new constituent is added to a mixed waste container, so that others in the laboratory will be aware and manage it accordingly.

Some common incompatible waste streams include:

- Oxidizers added to any fuel can create an exothermic reaction and explode. The most frequent is acids oxidizing flammable liquids. For this reason, all flammable liquids are pH tested before they are consolidated
- Piranha etch solution is a specific waste stream that contains sulfuric acid and hydrogen peroxide, which form a reactive mixture that is often still fuming during disposal. For this waste stream, and other reactive mixtures like it, vented caps are mandatory

WASTES THAT REQUIRE SPECIAL HANDLING

Unknowns

Unlabeled chemical containers and unknown/unlabeled wastes are considered unknowns, and additional fees must be paid to have these materials analyzed and identified. These containers must be labeled with the word "unknown".

Peroxide Forming Chemicals

Peroxide forming chemicals, or PFCs, include a number of substances that can react with air, moisture or product impurities, and undergo a change in their chemical composition during normal storage. The peroxides that form are highly reactive and can explode upon shock or spark. Peroxides are not particularly volatile and thus tend to precipitate out of liquid solutions. It is particularly dangerous to allow a container of these materials to evaporate to dryness, leaving the crystals of peroxide on the surfaces of the container.

Each container of peroxide forming chemicals should be dated with the <u>date received</u> and the <u>date</u> <u>first opened</u>. There are three classes of peroxide forming chemicals, with each class having different management guidelines. A guide to managing some PFCs commonly found in research labs is provided in *Appendix H*. Since this Appendix does not provide an exhaustive list of PFCs, review the safety information provided by the manufacturer for any chemicals you purchase.

Ensure containers of PFCs are kept tightly sealed to avoid unnecessary evaporation, as this inhibits the stabilizers that are sometimes added. Visually inspect containers periodically to ensure that they are free of exterior contamination or crystallization. PFC containers must be disposed of prior to expiration date. If old containers of peroxide forming chemicals are discovered in the laboratory, (greater than two years past the expiration date or if the date of the container is unknown), **do not handle the container**. If crystallization is present in or on the exterior of a container, **do not handle the container**. Secure it and contact EH&S, 4-6200 for pick-up and disposal.

Dry Picric Acid

Picric acid (also known as trinitrophenol) must be kept hydrated with deionized water at all times, as it becomes increasingly unstable as it loses water content. When dehydrated, it is not only explosive but also sensitive to shock, heat and friction. Picric acid is highly reactive with a wide variety of compounds (including many metals) and is extremely susceptible to the formation of picrate salts. Be sure to label all containers that contain picric acid with the date received, and then monitor the

water content every 6 months. Add deionized water as needed to maintain a consistent liquid volume.

If old or previously unaccounted for bottles of picric acid are discovered, **do not touch the container**. Depending on how long the bottle has been abandoned and the state of the product inside, even a minor disturbance could be dangerous. Visually inspect the contents of the bottle without moving it to evaluate its water content and look for signs of crystallization inside the bottle and around the lid. If there is even the slightest indication of crystallization, signs of evaporation, or the formation of solids in the bottle, **do not handle the container** and contact **EH&S**, **4-6200** immediately. Secure the area and restrict access to the container until it can be evaluated by EH&S personnel.

Explosives and Compounds with Shipping Restrictions

A variety of other compounds that are classified as explosives or are water or air reactive are used in research laboratories. These compounds often have shipping restrictions and special packaging requirements. When disposing of these compounds, employees must ensure that they are stored appropriately for transport. Flammable metals must be completely submerged in oil prior to disposal. Many pyrophoric and reactive compounds can be stabilized using a quenching procedure prior to disposal. Chemicals classified by the Department of Transportation (DOT) as explosives (e.g., many nitro- and azo-compounds)



will require special packaging and shipping, and may require stabilization prior to disposal. Consult with the Chemical Hygiene Officer and the Hazardous Waste Manager for disposal considerations of these compounds.

Chemotherapy Waste

Chemotherapy waste may be a hazardous chemical waste or biomedical waste. Proper classification is necessary to be in compliance with the laws regulating each waste type.

A number of chemotherapy drugs are regulated as a hazardous chemical waste. These include but are not limited to:

Chlorambucil	Diethylstilbestrol	Streptozotocin
Cyclophosphamide	Melphalan	Uracil mustard
Daunomycin	Mitomycin C	

Chemotherapy wastes that exhibit one or more of the EPA characteristics of a hazardous chemical waste are also regulated as a hazardous chemical waste. These characteristics are:

Corrosivity
 Ignitability
 Reactivity
 Toxicity

All chemotherapy waste that is also a hazardous chemical waste, in addition to bulk (pourable) chemotherapy waste such as full expired vials, must be managed according to the UCI Hazardous Waste Guidelines available online at www.ehs.uci.edu/programs/enviro/.

All other chemotherapy waste may be managed as a biomedical waste. This includes:

• Trace-contaminated items generated in the preparation and administration of antineoplastic / cytotoxic drugs. Some examples include:

Barriers	Gloves	Spill Clean-Up Material
Masks	Gowns	Empty Intravenous Bags/Bottles
Empty Drug Vials	IV Tubing	

Labeling Requirements For Trace Chemotherapy Waste:

- All trace chemotherapy waste must be placed in red bags and labeled with the words "BIOHAZARDOUS WASTE" or with the international symbol and the word "BIOHAZARD".
- All secondary containers of trace chemotherapy waste must be labeled with the words "CHEMOTHERAPY WASTE - FOR INCINERATION ONLY".

Trace Chemotherapy Waste Storage:

- All trace chemotherapy waste bags must be securely tied.
- Secondary containers must be rigid, leak resistant, have tight fitting covers, be clean, and in good repair.
- Trace chemotherapy waste must be transferred to EH&S within 7 calendar days of being generated.

Trace Chemotherapy Waste Disposal:

Request Pickup Service via the Internet:

- Visit www.ehs.uci.edu/programs/enviro/
- Fill out the "Biomedical Waste Collection" form.
- We will pick up your waste within 1-3 days.

MANAGING EMPTY CONTAINERS

At no time should full or partially full containers be placed in the regular trash.

Empty containers do not have to be managed as hazardous waste. To be considered empty:

- No material can be poured or scraped from a container.
- An aerosol container must have its contents and pressure completely dispensed, and the spray mechanism in place and functional.

Notes and Exceptions:

- All containers that once held acutely / extremely hazardous materials are considered hazardous waste and must be disposed of by EH&S.
- If an empty hazardous material container is greater than five gallons, it must be picked up by EH&S.

DISPOSAL

Request a pickup via the internet:

- Visit www.ehs.uci.edu/programs/enviro/
- Fill out the "Chemical Waste Collection" form.
- EH&S will pick up your waste within 1-3 days.

Do not dispose of chemicals by pouring them down the drain or placing them in the trash. Do not use fume hoods to evaporate chemicals.

Hazardous Waste Minimization

In order to reduce the amount of chemicals that become waste, administrative and operational waste minimization controls can be implemented. Usage of chemicals in the laboratory areas should be reviewed to identify practices which can be modified to reduce the amount of hazardous waste generated.

Purchasing Control: When ordering chemicals, be aware of any properties that may preclude long term storage, and order only exact volumes to be used. Using suppliers who can provide quick delivery of small quantities can assist with reducing surplus chemical inventory. Consider establishing a centralized purchasing program to monitor chemical purchases and avoid duplicate orders.

Inventory Control: Rotate chemical stock to keep chemicals from becoming outdated. Locate surplus/unused chemicals and attempt to redistribute these to other users.

Operational Controls: Review your experimental protocol to ensure that chemical usage is minimized. Reduce total volumes used in experiments; employ small scale procedures when possible. Instead of wet chemical techniques, use instrumental methods, as these generally require smaller quantities of chemicals. Evaluate the costs and benefits of off-site analytical services. Avoid mixing hazardous and non-hazardous waste streams. Use less hazardous or non-hazardous substitutes when feasible. Some examples include:

- Specialty detergents can be substituted for sulfuric acid/chromic acid cleaning solutions
- Gel Green and Gel Red are recommended in place of ethidium bromide

MERCURY THERMOMETER EXCHANGE PROGRAM

Cleaning up spilled mercury from a broken thermometer is the most frequent EH&S Haz Mat response. Mercury is a potent neurotoxin and environmental contaminant, and UC has a goal of having a mercury free campus. EH&S will exchange mercury thermometers with non-mercury thermometers free of charge. To request an exchange of mercury thermometers, fill out the form at: http://www.ehs.uci.edu/programs/enviro/MercuryFreeUCI.pdf

Chapter 10: Accidents and Chemical Spills

Overview

Laboratory emergencies may result from a variety of factors, including serious injuries, fires and explosions, spills and exposures, and natural disasters. All laboratory employees should be familiar with and aware of the location of their laboratory's emergency response procedures and safety manuals. **Before beginning any laboratory task**, know what to do in the event of an emergency situation. Identify the location of safety equipment, including first aid kits, eye washes, safety showers, fire extinguishers, fire alarm pull stations, and spill kits. Plan ahead and know the location of the closest fire alarms, exits, and telephones in your laboratory. The UCI Emergency Procedures flip chart (http://www.police.uci.edu/awareness/docs/UCI_EmerProc.pdf) provides an overview of emergency response procedures. It should be posted in each laboratory.

For all incidents requiring emergency response, call UCIPD at 911 from a campus phone.

Accidents

Pls/Laboratory Supervisors are responsible for ensuring that their employees receive appropriate medical attention in the event of an occupational injury or illness. Refer to the UC Irvine Injuries and Medical Treatment Poster (*Appendix N*) All accidents and near misses must be reported to **your supervisor and EH&S.** Report an injury, incident or safety concern to EH&S online at https://www.ehs.uci.edu/apps/hr/index.jsp. EH&S will conduct an accident investigation and develop recommendations and corrective actions to prevent future accidents. At a minimum, each laboratory must have the following preparations in place:

- Fully stocked first aid kit
- Posting of emergency telephone numbers and locations of emergency treatment facilities
- Training of adequate number of staff in basic CPR and first aid
- Training of staff to accompany injured personnel to medical treatment site and to provide medical personnel with copies of SDS(s) for the chemical(s) involved in the incident

Accident Prevention Methods		
Do	Don't	
 Always wear appropriate eye protection Always wear appropriate laboratory coat Always wear appropriate gloves Always wear closed-toe shoes and long pants Always confine long hair and loose clothing Always use the appropriate safety controls (e.g., certified fume hoods) Always label and store chemicals properly Always keep the work area clean and uncluttered 	 Never enter the laboratory wearing inappropriate clothing (e.g., open-toe shoes and shorts) Never work alone on procedures involving hazardous chemicals, biological agents, or other physical hazards Never eat, drink, chew gum or tobacco, smoke, or apply cosmetics in the laboratory Never use damaged glassware or other equipment 	

If an employee has a severe or life threatening injury, call for emergency response. Employees with minor injuries should be treated with first aid kits as appropriate, and sent to an Occupational Health Facility for further evaluation and treatment. After normal business hours, treatment can be obtained at designated medical centers and emergency rooms.

Serious occupational injuries, illnesses, and exposures to hazardous substances must be reported your supervisor and EH&S within 8 hours. EH&S will report the event to Cal/OSHA, investigate the accident, and complete exposure monitoring if necessary. Serious injuries include those that result in permanent impairment or disfigurement, or require hospitalization. Examples include amputations, lacerations with severe bleeding, burns, concussions, fractures and crush injuries. As soon as PIs/Laboratory Supervisors are aware of a potentially serious incident, they must contact EH&S. EH&S must ensure that all serious injuries are reported to Cal/OHSA within 8 hours.

Fire-Related Emergencies

If you encounter a fire, or a fire-related emergency (e.g., abnormal heating, smoke, burning odor), immediately follow these instructions:

- 1. Pull the fire alarm pull station **and call 911 from a campus phone or** from an offcampus or cell phone to notify the Fire Department;
- 2. Evacuate and isolate the area
 - Use portable fire extinguishers to facilitate evacuation and/or control a small fire (i.e., size of a small trash can), if safe to do so
 - If possible, shut off equipment before leaving
 - Close doors;
- 3. Remain safely outside the affected area to provide details to emergency responders; and
- 4. Evacuate the building when the alarm sounds. It is against state law to remain in the building when the alarm is sounding. If the alarm sounds due to a false alarm or drill, you will be allowed to re-enter the building as soon as the Fire Department determines that it is safe to do so. Do not go back in the building until the alarm stops and you are cleared to reenter.

If your clothing catches on fire, go to the nearest emergency shower immediately. If a shower is not immediately available, then stop, drop, and roll. A fire extinguisher may be used to extinguish a fire on someone's person. Report any burn injuries to the supervisor immediately and seek medical treatment. Report to your supervisor and EH&S within 8 hours every time a fire extinguisher is discharged.

Chemical Spills

Chemical spills can result in chemical exposures and contaminations. Chemical spills become emergencies when:

- The spill results in a release to the environment (e.g., sink or floor drain)
- The material or its hazards are unknown
- Laboratory staff cannot safety manage the hazard because the material is too hazardous or the quantity is too large

Effective emergency response to these situations is imperative to mitigate or minimize adverse reactions when chemical incidents occur. After emergency procedures are completed, all personnel involved in the incident should follow UCI chemical exposure procedures as appropriate (see *Chapter 5: Chemical Exposure Assessment*).

In the event of a significant chemical exposure or contamination, immediately try to remove or isolate the chemical if safe to do so.

Factors to Consider Before Spill Clean-Up

- 1. Size of spill area
- 2. Quantity of chemical
- 3. Toxicity
- 4. Volatility
- 5. Clean up materials available
- 6. Training of responders

When skin or eye exposures occur, remove contaminated clothing and flush the affected area using an eye wash or shower for at least 15 minutes. If a chemical is ingested, drink plenty of water. Obtain medical assistance as indicated. Remember to wear appropriate PPE before helping others. PIs/ Laboratory Supervisors must review all exposure situations, make sure affected employees receive appropriate medical treatment and/or assessment, and arrange for containment and clean-up of the chemical as appropriate.

Small chemical spills can be cleaned up by laboratory personnel who have been trained in spill clean up and with the appropriate materials. A small spill is generally defined as < 1 liter of chemical that is not highly toxic, does not present a significant fire or environmental hazard, and is not in a public area such as a common hallway. **Large chemical spills** include spills of larger quantities, spills of any quantity of highly toxic chemicals, or chemicals in public areas or adjacent to drains. Large spills require emergency response. Call **911 from a campus phone or** from an off-campus or cell phone for assistance.

WHAT TO DO WITH A SMALL CHEMICAL SPILL (<1 LITER)

- Evacuate all non-essential persons from the spill area
- If needed, call for medical assistance by dialing **911** from a campus phone or from an off-campus or cell phone
- Help anyone who may have been contaminated. Use emergency eyewashes/showers by flushing the skin or eyes for *at least 15 minutes*
- Post someone just outside the spill area to keep people from entering. Avoid walking through contaminated areas
- You must have the proper protective equipment and clean-up materials to clean-up spills. Check the chemical's Safety Data Sheet (SDS) in your laboratory or online (*http://www.ucmsds.com*) for spill clean-up procedures, or call EH&S for advice
- Turn off sources of flames, electrical heaters, and other electrical apparatus, and close valves on gas cylinders if the chemical is flammable



- Confine the spill to a small area. Do not let it spread
- Avoid breathing vapors from the spill. If the spill is in a non-ventilated area, do not attempt to clean it up. Call for emergency personnel to respond and clean up the spill
- Wear personal protective equipment, including safety goggles, gloves, and a laboratory coat or other protective garment to clean-up the spill
- Work with another person to clean-up the spill. Do not clean-up a spill alone
- DO NOT ADD WATER TO THE SPILL
- Use an appropriate kit to neutralize and absorb inorganic acids and bases. For other chemicals, use the appropriate kit or absorb the spill with sorbent pads, paper towels, vermiculite, dry sand, or diatomaceous earth. For mercury spills and specific procedures for all other spills see *Appendix M.*

Collect the residue and place it in a clear plastic bag. Double bag the waste and label the bag with the contents. Fill out the "Chemical Waste Collection" form to request a pickup via the internet at http://www.ehs.uci.edu/programs/enviro/

WHAT TO DO WITH A LARGE CHEMICAL SPILL (>1 LITER)

Large chemical spills require emergency response. Call 911 from a campus phone or from an off-campus or cell phone. If the spill presents a situation that is immediately dangerous to life or health (IDLH) or presents a significant fire risk, activate a fire alarm, evacuate the area and wait for emergency response to arrive.

- Evacuate all non-essential persons from the spill area
- Call for emergency response/medical assistance by dialing **911**
- Remove the injured and/or contaminated person(s) and provide first aid
- Help anyone who may have been contaminated. Use emergency eyewashes/showers by flushing the skin or eyes for *at least 15 minutes*
- As you evacuate the laboratory, close the door behind you, and:
 - Post someone safely outside and away from the spill area to keep people from entering
 - Confine the spill area if possible and safe to do so
 - Leave on exhaust ventilation
 - If possible, turn off all sources of flames, electrical heaters, and other electrical equipment if the spilled material is flammable
 - Avoid walking through contaminated areas or breathing vapors of the spilled material
- Any employee with known contact with a particularly hazardous chemical must shower, including washing of the hair as soon as possible unless contraindicated by physical injuries

Highly Toxic Chemical Spills Do no try to clean up spills of any size. All spills require emergency response: • Aromatic amines • Hydrazine • Bromines • Nitriles • Carbon disulfide • Nitro-compounds • Cyanides • Organic halides

Ethers

Appendices

Appendix A: General Rules for Laboratory Work with Chemicals

PRUDENT LABORATORY PRACTICES

It is prudent to minimize all chemical exposures. Few laboratory chemicals are without hazards, and general precautions for handling all laboratory chemicals should be adopted, in addition to specific guidelines for particular chemicals. Exposure should be minimized even for substances of no known significant hazard, and special precautions should be taken for work with substances that present special hazards. One should assume that any mixture will be more toxic than its most toxic component and that all substances of unknown toxicity are toxic.

Avoid inadvertent exposures to hazardous chemicals by developing and encouraging safe habits and thereby promoting a strong safety culture.

SAFE LABORATORY HABITS

Personal Protective Equipment:

- Wear closed-toe shoes and full length pants, or equivalent as identified by the laboratory PPE Assessment, at all times when in the laboratory
- Utilize appropriate PPE while in the laboratory and while performing procedures that involve the use of hazardous chemicals or materials. These items may include laboratory coats, gloves, and safety glasses or goggles. Visit http://www.ehs.uci.edu/PPE.html.
- Confine long hair and loose clothing
- Wear appropriate gloves when the potential for contact with toxic materials exists; inspect the gloves before each use, and replace them often
- Remove laboratory coats or gloves immediately on significant contamination, as well as before leaving the laboratory
- Avoid use of contact lenses in the laboratory unless necessary; if they are used, inform supervisor so special precautions can be taken
- Ensure that appropriate PPE is worn by all persons, including visitors, where chemicals are stored or handled
- Use appropriate respiratory equipment when air contaminant concentrations are not sufficiently restricted by engineering controls, inspecting the respirator before use. Use of respirators requires a respirator hazard assessment and successful completion of the EH&S Respirator Training and Fit Test course. Visit UCI's Respiratory Protection Program at http://www.ehs.uci.edu/programs/ih/respiratory.html.
- Use any other protective and emergency apparel and equipment as appropriate. Be aware of the locations of first aid kits and emergency eyewash and shower stations

Chemical Handling:

- Use only those chemicals for which the quality of the available ventilation system is appropriate
- Vent apparatus which may discharge toxic chemicals (vacuum pumps, distillation columns, etc.) into local exhaust devices
- Properly label and store all chemicals. Use secondary containment at all times
- Deposit chemical waste in appropriately labeled receptacles and follow all other waste disposal procedures of the Chemical Hygiene Plan
- In the case of an accident or spill, refer to the emergency response procedures for the specific material. These procedures should be readily available to all personnel. Information on minor chemical spill mitigation may also be referenced in *Appendix M*. For general guidance, the following situations should be addressed:
 - Eve Contact: Promptly flush eyes with water for a prolonged period (15 minutes) and seek medical attention
 - <u>Skin Conta</u>ct: Promptly flush the affected area with water and remove any contaminated clothing. If symptoms persist after washing, seek medical attention
 - <u>Clean-up</u>: Promptly clean up spills, using appropriate protective apparel and equipment, and proper disposal

Equipment Storage and Handling:

- Use equipment only for its designed purpose
- Store laboratory glassware with care to avoid damage. Use extra care with Dewar flasks and other evacuated glass apparatus; shield or wrap them to contain chemicals and fragments should implosion occur
- Use certified fume hoods, glove boxes, or other ventilation devices for operations which might result in release of toxic chemical vapors or dust. Preventing the escape of these types of materials into the working atmosphere is one of the best ways to prevent exposure
- Keep hood closed at all times, except when adjustments within the hood are being made
- Leave the fume hood "on" even when it is not in active use if toxic substances are in the fume hood or if it is uncertain whether adequate general laboratory ventilation will be maintained when it is "off"

Laboratory Operations:

- Keep the work area clean and uncluttered
- Seek information and advice about hazards, plan appropriate protective procedures, and plan positioning of equipment before beginning any new operation
- If unattended operations are unavoidable, and have been approved by the PI/Laboratory Supervisor, place an appropriate sign on the door, leave lights on, and provide for containment of toxic substances in the event of failure of a utility service (such as cooling water)
- Be alert to unsafe conditions and ensure that they are corrected when detected

UNSAFE LABORATORY HABITS

Personal Protective Equipment:

• Do not enter the laboratory without wearing appropriate clothing, including closed-toe shoes and full length pants, or equivalent. The area of skin between the shoe and ankle should not be exposed. Do not wear laboratory coats or gloves outside of the laboratory area

Chemical Handling:

- Do not smell or taste chemicals.
- Do not allow release of toxic substances or fumes into cold or warm rooms, as these types of areas typically involve re-circulated atmospheres
- Never use mouth suction for pipeting or starting a siphon
- Do not dispose of any hazardous chemicals through the sewer system. These substances might interfere with the biological activity of waste water treatment plants, create fire or explosion hazards, cause structural damage or obstruct flow

Equipment Storage and Handling:

- Do not use damaged glassware or other equipment, under any circumstances. The use of damaged glassware increases the risks of implosion, explosion, spills, and other accidents
- Do not use uncertified fume hoods or glove boxes for hazardous chemical handling
- Avoid storing materials in hoods and do not allow them to block vents or air flow

Laboratory Operations:

- Never work alone on procedures involving hazardous chemicals, biological agents, or other physical hazards
- Avoid unattended operations, if at all possible. Unattended operations require prior approval from the PI/Laboratory Supervisor
- Do not engage in distracting behavior such as practical joke playing in the laboratory. This type of conduct may confuse, startle, or distract another worker

Food/Drink:

- Do not eat, drink, smoke, chew gum, or apply cosmetics in areas where laboratory chemicals are present; wash hands before conducting these activities
- Do not store, handle, or consume food or beverages in storage areas, refrigerators, glassware or utensils which are also used for laboratory operations
- Wash areas of exposed skin well before leaving the laboratory

Appendix B: Sample Safety Data Sheet (SDS)

Science Lab Com Chemicals & Laboratory Equipment	2 3 0 Health 3 Fire 2 Reactivity 0 Personal G Protection G		
Material Safety Data Sheet Formaldehyde 37% solution MSDS Section 1: Chemical Product and Company Identification			
	Contact Information:		
Product Name: Formaldehyde 37% solution Catalog Codes: SLF1428	Sciencelab.com, Inc. 14025 Smith Rd.		
CAS#: Mixture. RTECS: LP8925000	Houston, Texas 77396 US Sales: 1-800-901-7247 International Sales: 1-281-441-4400		
TSCA: TSCA 8(b) inventory: Formaldehyde; Methyl alcohol: Water	Order Online: ScienceLab.com		
CI#: Not applicable.	CHEMTREC (24HR Emergency Telephone), call: 1-800-424-9300		
Synonym: Formalin	International CHEMTREC, call: 1-703-527-3887		
Chemical Name: Formaldehyde Chemical Formula: HCHO	For non-emergency assistance, call: 1-281-441-4400		
Section 2: Composition and Information on Ingredients			

Composition:

Name	CAS #	% by Weight
Formaldehyde	50-00-0	36.5-38
Methyl alcohol	67-56-1	10-15
Water	7732-18-5	47-53.5

Toxicological Data on Ingredients: Formaldehyde: ORAL (LD50): Acute: 100 mg/kg [Rat]. 42 mg/kg [Mouse]. 260 mg/kg [Guinea pig]. MIST (LC50): Acute: 454000 mg/m 4 hours [Mouse]. Methyl alcohol: ORAL (LD50): Acute: 5628 mg/kg [Rat]. DERMAL (LD50): Acute: 15800 mg/kg [Rabbit]. VAPOR (LC50): Acute: 64000 ppm 4 hours [Rat].

Section 3: Hazards Identification

Potential Acute Health Effects:

Very hazardous in case of eye contact (irritant), of ingestion, . Hazardous in case of skin contact (irritant, sensitizer, permeator), of eye contact (corrosive). Slightly hazardous in case of skin contact (corrosive). Severe over-exposure can result in death. Inflammation of the eye is characterized by redness, watering, and itching.

Potential Chronic Health Effects:

Hazardous in case of skin contact (sensitizer). CARCINOGENIC EFFECTS: Classified A2 (Suspected for human.) by ACGIH, 2A (Probable for human.) by IARC [Formaldehyde]. MUTAGENIC EFFECTS: Mutagenic for mammalian somatic cells. [Formaldehyde]. Mutagenic for mammalian somatic cells. [Methyl

Sample SDS, cont.

alcohol]. Mutagenic for bacteria and/or yeast. [Methyl alcohol]. TERATOGENIC EFFECTS: Classified POSSIBLE for human [Methyl alcohol]. DEVELOPMENTAL TOXICITY: Not available The substance may be toxic to kidneys, liver, skin, central nervous system (CNS). Repeated or prolonged exposure to the substance can produce target organs damage. Repeated exposure to a highly toxic material may produce general deterioration of health by an accumulation in one or many human organs.

Section 4: First Aid Measures

Eye Contact:

Check for and remove any contact lenses. Immediately flush eyes with running water for at least 15 minutes, keeping eyelids open. Cold water may be used. Get medical attention immediately.

Skin Contact:

In case of contact, immediately flush skin with plenty of water. Cover the irritated skin with an emollient. Remove contaminated clothing and shoes. Cold water may be used. Wash clothing before reuse. Thoroughly clean shoes before reuse. Get medical attention.

Serious Skin Contact:

Wash with a disinfectant soap and cover the contaminated skin with an anti-bacterial cream. Seek immediate medical attention.

Inhalation:

If inhaled, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention immediately.

Serious Inhalation:

Evacuate the victim to a safe area as soon as possible. Loosen tight clothing such as a collar, tie, belt or waistband. If breathing is difficult, administer oxygen. If the victim is not breathing, perform mouth-to-mouth resuscitation. WARNING: It may be hazardous to the person providing aid to give mouth-to-mouth resuscitation when the inhaled material is toxic, infectious or corrosive. Seek immediate medical attention.

Ingestion:

If swallowed, do not induce vomiting unless directed to do so by medical personnel. Never give anything by mouth to an unconscious person. Loosen tight clothing such as a collar, tie, belt or waistband. Get medical attention immediately.

Serious Ingestion: Not available.

Section 5: Fire and Explosion Data

Flammability of the Product: Flammable.

Auto-Ignition Temperature: 430°C (806°F)

Flash Points: CLOSED CUP: 50°C (122°F). OPEN CUP: 60°C (140°F).

Flammable Limits: The greatest known range is LOWER: 6% UPPER: 36.5% (Methyl alcohol)

Products of Combustion: These products are carbon oxides (CO, CO2).

Fire Hazards in Presence of Various Substances:

Flammable in presence of open flames and sparks, of heat. Non-flammable in presence of shocks, of oxidizing materials, of reducing materials, of combustible materials, of organic materials, of metals, of acids, of alkalis.

Explosion Hazards in Presence of Various Substances: Non-explosive in presence of open flames and sparks, of shocks.

Fire Fighting Media and Instructions:

Flammable liquid, soluble or dispersed in water. SMALL FIRE: Use DRY chemical powder. LARGE FIRE: Use alcohol foam, water spray or fog. Cool containing vessels with water jet in order to prevent pressure build-up, autoignition or explosion.

Special Remarks on Fire Hazards:

Explosive in the form of vapor when exposed to heat or flame. Vapor may travel considerable distance to source of ignition and flash back. When heated to decomposition, it emits acrid smoke and irritating fumes. CAUTION: MAY BURN WITH NEAR INVISIBLE FLAME (Methyl alcohol)

Special Remarks on Explosion Hazards:

Reaction with peroxide, nitrogen dioxide, and permformic acid can cause an explosion. (Formaldehyde gas)

Section 6: Accidental Release Measures

Small Spill:

Dilute with water and mop up, or absorb with an inert dry material and place in an appropriate waste disposal container. If necessary: Neutralize the residue with a dilute solution of sodium carbonate.

Large Spill:

Flammable liquid. Poisonous liquid. Keep away from heat. Keep away from sources of ignition. Stop leak if without risk. Absorb with DRY earth, sand or other non-combustible material. Do not get water inside container. Do not touch spilled material. Use water spray to reduce vapors. Prevent entry into sewers, basements or confined areas; dike if needed. Call for assistance on disposal. Neutralize the residue with a dilute solution of sodium carbonate. Be careful that the product is not present at a concentration level above TLV. Check TLV on the MSDS and with local authorities.

Section 7: Handling and Storage

Precautions:

Keep away from heat. Keep away from sources of ignition. Ground all equipment containing material. Do not ingest. Do not breathe gas/fumes/ vapor/spray. In case of insufficient ventilation, wear suitable respiratory equipment. If ingested, seek medical advice immediately and show the container or the label. Avoid contact with skin and eyes. Keep away from incompatibles such as oxidizing agents, reducing agents, acids, alkalis, moisture.

Storage:

Store in a segregated and approved area. Keep container in a cool, well-ventilated area. Keep container tightly closed and sealed until ready for use. Avoid all possible sources of ignition (spark or flame).

Section 8: Exposure Controls/Personal Protection

Engineering Controls:

Provide exhaust ventilation or other engineering controls to keep the airborne concentrations of vapors below their respective threshold limit value. Ensure that eyewash stations and safety showers are proximal to the work-station location.

Personal Protection:

Safety glasses. Lab coat. Vapor respirator. Be sure to use an approved/certified respirator or equivalent. Gloves (impervious).

Personal Protection in Case of a Large Spill:

Splash goggles. Full suit. Vapor respirator. Boots. Gloves. A self contained breathing apparatus should be used to avoid inhalation of the product. Suggested protective clothing might not be sufficient; consult a specialist BEFORE handling this product.

Exposure Limits:

Formaldehyde gas STEL: 0.3 (ppm) from ACGIH (TLV) [United States] STEL: 0.37 (mg/m3) from ACGIH (TLV) [United States] TWA: 0.75 STEL: 2 (ppm) from OSHA (PEL) [United States] TWA: 2 STEL: 2 (ppm) [United Kingdom (UK)] TWA: 2.5 STEL: 2.5 (mg/m3) [United Kingdom (UK)] Methyl alcohol TWA: 200 from OSHA (PEL) [United States] TWA: 200 STEL: 250 (ppm) from ACGIH (TLV) [United States] [1999] STEL: 250 from NIOSH [United States] TWA: 200 STEL: 250 (ppm) from NIOSH SKIN TWA: 200 STEL: 250 (ppm) [Canada] Consult local authorities for acceptable exposure limits.

Section 9: Physical and Chemical Properties

Physical state and appearance: Liquid.

Odor: Pungent. Suffocating. (Strong.)

Taste: Not available.

Sample SDS, cont.

Molecular Weight: 30.02

Color: Clear Colorless.

pH (1% soln/water): 3 [Acidic.] pH of the solution as is.

Boiling Point: 98°C (208.4°F)

Melting Point: -15°C (5°F)

Critical Temperature: The lowest known value is 240°C (464°F) (Methyl alcohol).

Specific Gravity: 1.08 (Water = 1)

Vapor Pressure: 2.4 kPa (@ 20°C)

Vapor Density: 1.03 (Air = 1)

Volatility: 100% (w/w).

Odor Threshold: The highest known value is 100 ppm (Methyl alcohol)

Water/Oil Dist. Coeff.: Not available.

Ionicity (in Water): Non-ionic.

Dispersion Properties: See solubility in water, diethyl ether, acetone.

Solubility:

Easily soluble in cold water, hot water. Soluble in diethyl ether, acetone, alcohol

Section 10: Stability and Reactivity Data

Stability: The product is stable.

Instability Temperature: Not available.

Conditions of Instability: Heat, ignition sources (flames, sparks), incompatible materials

Incompatibility with various substances:

Reactive with oxidizing agents, reducing agents, acids, alkalis. Slightly reactive to reactive with metals.

Corrosivity: Non-corrosive in presence of glass.

Special Remarks on Reactivity:

Also incompatible with urea, phenol, isocyanates, anhydrides, amines, AZO compounds, carbonyl compounds, oxides(e.g. nitrogen dioxide), performic acid, dithiocarbmates, or peroxides. Polymerization can be inhibited by the addition of methanol or stabilizers such as hydorxypropyl methyl cellulose, methyl ethyl celluloses, or isophthalobisguanamine.

Special Remarks on Corrosivity: Not available.

Polymerization: Will not occur.

Section 11: Toxicological Information

Routes of Entry: Absorbed through skin. Dermal contact. Eye contact. Inhalation.

Toxicity to Animals:

Acute oral toxicity (LD50): 42 mg/kg [Mouse]. (Formaldehyde) Acute dermal toxicity (LD50): 15800 mg/kg [Rabbit]. (Methyl alcohol). Acute toxicity of the mist(LC50): 454000 mg/m 4 hours [Mouse]. (Formaldehyde) 3

Chronic Effects on Humans:

CARCINOGENIC EFFECTS: Classified A2 (Suspected for human.) by ACGIH, 2A (Probable for human.) by IARC [Formaldehyde]. MUTAGENIC EFFECTS: Mutagenic for mammalian somatic cells. [Formaldehyde]. Mutagenic for bacteria and/or yeast. [Formaldehyde]. Mutagenic for mammalian somatic cells. [Methyl alcohol]. Mutagenic for bacteria and/or yeast. [Methyl alcohol]. TERATOGENIC EFFECTS: Classified POSSIBLE for human [Methyl alcohol]. DEVELOPMENTAL TOXICITY: Not available May cause damage to the following organs: kidneys, liver, central nervous system (CNS).

Other Toxic Effects on Humans:

Very hazardous in case of ingestion, . Hazardous in case of skin contact (irritant, sensitizer, permeator), of eye contact (corrosive), of inhalation (lung corrosive). Slightly hazardous in case of skin contact (corrosive).

Special Remarks on Toxicity to Animals:

Formaldehyde: LD50 [Rabbit] - Route: Skin; Dose: 270 ul/kg

Special Remarks on Chronic Effects on Humans:

Exposure to Formaldehyde and Methanol may affect genetic material (mutagenic). Exposure to Formaldehyde and Methanol may cause adverse reproductive effects and birth defects(teratogenic). Adverse reproductive effects of Formaldehyde as well as Methanol are primarily based on animal studies. Very few human studies have been done on the adverse reproductive effects from exposure to Formaldehyde. Studies produced a weak association (limited evidence) between adverse human female reproductive effects and occupational exposure. Furthermore, no human data could be found on adverse reproductive effects from occupational exposure to Methanol. Exposure to Formaldehyde may cause cancer.

Special Remarks on other Toxic Effects on Humans:

Acute Potential Health Effects: Skin: Corrosive. Causes skin irritation which may range from mild to severe with possible burns depending on the extent of exposure and concentration of solution. Other symptoms may include brownish discoloration of the skin, urticaria, and pustulovesicffular eruptions. May be absorbed through skin with symptoms paralleling those of ingestion. Eyes: Corrosive. Contact with liquid causes severe eye irritation and burns. It may cause irreversible eye damage (severe corneal Solutions containing low formaldehyde concentrations may produce transient discomfort and irritation. Inhalation: Causes irrititation of the respiratory tract (nose, throat, airways). Symptoms may include dry and sore mouth and throat, thirst, and sleep disturbances, difficulty breathing, shortness of breath, coughing, sneezing, wheezing rhinitis, chest tightness, pulmonary edema, bronchitis, tracheitis, laryngospasm, pneumonia, palpitations. It may also affect metabolism weight loss, metabolic acidosis), behavior/central nervous system (excitement, central nervous system depression, somnolence, convulsions, stupor, aggression, headache, weakness, dizziness, drowsiness, coma), peripheral nervous system, and blood. Ingestion: Harmful if swallowed. May be fatal. Causes gastrointestinal irritation with nausea, vomiting (possibly with blood), diarrhea, severe pain in mouth, throat and stomach, and possible corrosive injury to the gastrointestinal mucosa/ulceration or bleeding from stomach. May also affect the liver(jaundice), urinary system/kidneys (difficulty urinating, albuminuria, hematuria, anuria), blood, endocrine system, respiration (respiratory obstruction, pulmonary edema, bronchiolar obstruction), cardiovascular system (hypotension), metabolism (metabolic acidosis), eyes (retinal changes, visual field changes), and behavior/central nervous system (symptoms similar to those for inhalation). Contains Methanol which may cause blindness if swallowed. Chronic Potential Health Effects: Skin: Prolonged or repeated exposure may cause contact dermatits both irritant and allergic. It may also cause skin discoloration. Inhalation: Although there is no clear evidence, prolonged or repeated exposure may induce allergic asthma. Other effects are similar to that of acute exposure. Ingestion: Prolonged or repeated ingestion may cause gastrointestinal tract irritation and ulceration or bleeding from the stomach. Other effects may be similar to that of acute ingestion.

Section 12: Ecological Information

Ecotoxicity: Not available.

BOD5 and COD: Not available.

Products of Biodegradation:

Possibly hazardous short term degradation products are not likely. However, long term degradation products may arise.

Toxicity of the Products of Biodegradation: The products of degradation are less toxic than the product itself.

Special Remarks on the Products of Biodegradation:

Methanol in water is rapidly biodegraded and volatilized. Aquatic hydrolysis, oxidation, photolysis, adsorption to sediment, and bioconcentration are not significant fate processes. The half-life of methanol in surfact water ranges from 24 hrs. to 168 hrs. Based on its vapor pressure, methanol exists almost entirely in the vapor phase in the ambient atmosphere. It is degraded by reaction with photochemically produced hydroxyl radicals and has an estimated half-life of 17.8 days. Methanol is physically removed from air by rain due to its solubility. Methanol can react with NO2 in pollulted to form methyl nitrate. The half-life of methanol in air ranges from 71 hrs. (3 days) to 713 hrs. (29.7 days) based on photooxidation half-life in air. (Methyl alcohol)

Section 13: Disposal Considerations

Waste Disposal:

Waste must be disposed of in accordance with federal, state and local environmental control regulations.

Section 14: Transport Information

DOT Classification:

CLASS 3: Flammable liquid. Class 8: Corrosive material

Identification: : Formaldehyde Solution, flammable (Methyl alcohol) UNNA: 1198 PG: III

Special Provisions for Transport: Not available.

Section 15: Other Regulatory Information

Federal and State Regulations:

California prop. 65: This product contains the following ingredients for which the State of California has found to cause cancer, birth defects or other reproductive harm, which would require a warning under the statute: Formaldehyde California prop. 65 (no significant risk level): Formaldehyde: 0.04 mg/day (inhalation) California prop. 65: This product contains the following ingredients for which the State of California has found to cause cancer which would require a warning under the statute: Formaldehyde Solution Connecticut hazardous material survey.: Formaldehyde; Methyl alcohol Illinois toxic substances disclosure to employee act: Formaldehyde; Methyl alcohol Illinois chemical safety act: Formaldehyde; Methyl alcohol New York release reporting list. Formaldehyde; Methyl alcohol Rhode Island RTK hazardous substances: Formaldehyde; Methyl alcohol Pennsylvania RTK: Formaldehyde; Methyl alcohol Minnesota: Formaldehyde gas; Methyl alcohol Massachusetts RTK: Formaldehyde; Methyl alcohol Massachusetts spill list: Formaldehyde; Methyl alcohol New Jersey: Formaldehyde; Methyl alcohol New Jersey spill list: Formaldehyde; Methyl alcohol Louisiana RTK reporting list. Formaldehyde; Methyl alcohol California Director's List of Hazardous Substances: Formaldehyde; Methyl alcohol TSCA 8(b) inventory: Formaldehyde gas; Methyl alcohol; Water TSCA 4(f) priority risk review: Formaldehyde, Reagnt, ACS SARA 302/304/311/312 extremely hazardous substances: Formaldehyde SARA 313 toxic chemical notification and release reporting: Formaldehyde; Methyl alcohol CERCLA: Hazardous substances.: Formaldehyde: 100 lbs. (45.36 kg); Methyl alcohol: 5000 lbs. (2268 kg);

Other Regulations:

OSHA: Hazardous by definition of Hazard Communication Standard (29 CFR 1910.1200). EINECS: This product is on the European Inventory of Existing Commercial Chemical Substances.

Other Classifications:

WHMIS (Canada):

CLASS B-3: Combustible liquid with a flash point between 37.8°C (100°F) and 93.3°C (200°F). CLASS D-1A: Material causing immediate and serious toxic effects (VERY TOXIC). CLASS D-2A: Material causing other toxic effects (VERY TOXIC).

- DSCL (EEC):
- HMIS (U.S.A.):
 - Health Hazard: 3

Fire Hazard: 2

Reactivity: 0

Personal Protection: G

National Fire Protection Association (U.S.A.):

Health: 3

Flammability: 2

Reactivity: 0

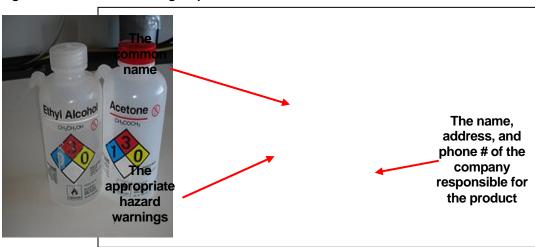
Specific hazard:

Sample SDS, cont.

	Section 16: Other Information
References: Not av	ailable.
Other Special Con	siderations: Not available.
Created: 10/09/200	5 05:35 PM
Last Updated: 11/0	1/2010 12:00 PM
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Appendix C: Container Labeling

Chemical container labels are a good resource for information on chemical hazards. All containers of hazardous chemicals must have labels attached. Figure C.1 displays the label requirements.





The warning may be a single word (e.g. Danger, Caution, Warning) or may identify the primary hazards, including both physical (e.g. water reactive, flammable, or explosive) and health (e.g. carcinogen, corrosive or irritant), such as what is found on an NFPA diamond and hazard warnings from the label or SDS.

Most labels provide additional safety information to help workers protect themselves from the substance. This information may include protective measures and/or protective clothing to be used, first aid instructions, storage information and emergency procedures.

Chemical Labeling – What are Laboratory Personnel Responsible for?

- Inspecting incoming containers to be sure that labels are attached and are in good condition and contain the information outlined above
- Reading the container label each time a newly purchased chemical is used. It is possible that the
 manufacturer may have added new hazard information or reformulated the product since the last
 purchase
- Ensuring that chemical container labels are not removed or defaced, except when containers are empty
- Labeling any secondary containers used in the laboratory, to prevent unknown chemicals or inadvertent reaction
- Verifying that chemical waste containers have complete and accurate chemical waste labels

Labeling is important for the safe management of chemicals, preventing accidental misuse, inadvertent mixing of incompatible chemicals, and facilitating proper chemical storage. Proper labeling helps ensure quick response in the event of an accident, such as a chemical spill or chemical exposure incident. Finally, proper labeling prevents the high costs associated with disposal of "unknown" chemicals.

With the exception of transient containers that will contain chemicals for immediate use, all containers of chemicals being used or generated in UC research laboratories must be labeled sufficiently to indicate the contents of the container. On original containers, the label must not be removed or defaced in any way until the container is emptied of its original contents. Incoming containers must be inspected to make sure the label is in good condition. It is also advisable to put a date on new chemicals when they are received in the laboratory, and to put a date on containers of chemicals generated in the laboratory, as well as the initials of the responsible person.

Abbreviations or other acronyms may be used to label containers of chemicals generated in the laboratory as long as all personnel working in the laboratory understand the meaning of the label, or know the location of information, such as a laboratory notebook or log sheet that contains the code associated with content information. In addition, small containers, such as vials and test tubes, can be labeled as a group by labeling the outer container (e.g., rack or box). Alternatively, a placard can be used to label the storage location for small containers (e.g., shelf, refrigerator, etc.). This information must be provided to janitorial and maintenance staff as part of their hazard communication training.

Containers of practically non-toxic and relatively harmless chemicals must also be labeled with content information, <u>including containers such as squirt bottles containing water</u>.

With respect to chemical labeling, all potentially hazardous chemicals transferred from their original container to a second container must be labeled with the chemical name and the principal hazards found on the primary container label or SDS. For more information on labeling, see Chapter 6: Labeling, Storage, Inventory and Transport.

Appendix D: SOP Instructions and Template

INSTRUCTIONS FOR COMPLETING STANDARD OPERATING PROCEDURES

To be in compliance with the Cal/OSHA Laboratory Standard, laboratory-specific Standard Operating Procedures (SOPs) are required to be included in your Chemical Hygiene Plan. This manual does not provide specific SOPs for the hazardous chemical or hazardous substance use operations or procedures in your particular laboratory. If your laboratory research involves the use of hazardous substances or chemicals, you must develop laboratory-specific SOPs to supplement the information found in the EH&S Laboratory Safety Manual and Chemical Hygiene Plan. You may work with your departmental safety committee and EH&S, as required. Below are instructions for completing the laboratory-specific SOPs with the corresponding template. Please contact the campus Chemical Hygiene Officer with any questions or comments you may have while completing your SOPs. Completed SOPs are reviewed by EH&S during annual inspections.

A UCI SOP template and signature page are available at:

http://www.ehs.uci.edu/programs/sop_library/UCSOPtemplate.docm

http://www.ehs.uci.edu/programs/sop_library/SOPTemplateAcknowledgementSignatureUCI.docx

1. Type of SOP

- **Process**: the SOP will be for a process such as distillation, synthesis, etc.
- **Hazardous chemical**: the SOP will be for an individual chemical such as arsenic, formaldehyde, nitric acid, etc.
- **Hazard class:** the SOP will be for a hazard class of chemicals such as oxidizer, flammable, corrosive, etc.

2. Describe the Process, Hazardous Chemical or Hazard Class

- **Process**: Briefly describe the process and name all the hazardous chemicals or substances used in the process (see Hazardous Operations SOPs at http://www.ehs.uci.edu/programs/sop_library/index.html#HazOps)
- **Hazardous chemical**: Provide the name of the chemical. Include the full name, common name, and any abbreviations used for the chemical (see Hazardous Material SOPs at http://www.ehs.uci.edu/programs/sop_library/index.html#HazMat)
- **Hazard class:** Name the hazard class and list the name of the chemicals in this hazard class used or stored in your laboratory (see Hazardous Material Class SOPs at http://www.ehs.uci.edu/programs/sop library/index.html#HazMatClassSOPs)

3. Potential Hazards

Describe all the potential hazards for each process, hazardous chemical, or hazard class. Describe the potential for both physical and health hazards. Health hazards include carcinogens, toxic or highly toxic agents, reproductive toxins, irritants, corrosives, sensitizers, hepatotoxins, nephrotoxins, neurotoxins, agents which act on the hematopoietic systems, and agents which damage the lungs, skin, eyes, or mucous membranes. State the potential for chronic and/or acute health hazard effects of the chemical(s).

Physical hazards include radioactivity, cryogen, high temperature, electrical, compressed gas or other pressure systems, UV light, laser, flammable or combustible, corrosive, water-reactive, unstable, oxidizer, pyrophoric, explosive, or peroxide formers.

4. Circumstances Requiring Prior Approval

Discuss the circumstances under which this particular process, hazardous chemical or hazard class will require prior approval (if any) from the PI/Laboratory Supervisor or Chemical Hygiene Officer. The circumstances may be based on such criteria as: the inherent hazards of the material(s) used, the hazards of the experimental process, the experience level of the worker, the scale of the reaction, etc. Some examples of circumstances that may require prior approval include unattended or overnight operations, use of explosives or pyrophorics, use of highly toxic gas in any amount, use of large quantities of toxic or corrosive gases or use of carcinogens.

5. Personal Protective Equipment (PPE)

Identify the required PPE for the process, hazardous chemical, or hazard class. PPE includes, but is not limited to: gloves, aprons, laboratory coats, safety glasses, goggles, masks, respirators, or face shields.

6. Engineering Controls

Describe or list engineering controls that will be used to prevent or reduce employee exposure to hazards. Examples of engineering controls are fume hoods, glove boxes, interlocks on equipment, and shielding of various kinds.

7. Special Handling and Storage Requirements

Describe the storage requirements for hazardous substances, including special containment devices, special temperature requirements, special storage areas or cabinets, chemical compatibility storage requirements, etc. State the policy regarding access to the substance(s). Provide the exact storage location in the laboratory. Describe any special procedures, such as dating peroxide forming chemicals on receipt, opening and disposal, or testing after an appropriate amount of time has passed. Describe safe methods of transport, such as in a secondary container using a low, stable cart, or using two hands to carry the chemical container.

8. Spill and Accident Procedures

Describe special procedures for spills, releases or exposures (e.g., neutralizing agents, use of fluorescence to detect materials, etc.). Indicate how spills, accidental releases and exposures will be handled. List location of the following emergency equipment: chemical spill clean-up kit, first-aid kit, emergency shower, eyewash, and fire extinguisher.

9. Decontamination Procedures

Describe specific decontamination procedures for equipment, glassware or work areas.

10. Waste Disposal Procedures

Describe the anticipated waste products as well as how waste will be collected and disposed.

11. Designated Area

Indicate the designated area established for experiments using particularly hazardous substances (PHS). A portion of a laboratory bench, a piece of equipment, the fume hood, or the entire laboratory may be considered as a designated area for experiments using PHS.

12. Safety Data Sheet (SDS) Location

State where the SDSs are kept for the chemicals, or hazardous substances, used in the laboratory. Indicate the location of other pertinent safety information (e.g., references, equipment manuals, etc.).

13. Protocols

Insert a copy of your specific laboratory procedures for the process, hazardous chemical or hazard class.

SOP TEMPLATE

Standard Operating Procedures Laboratory Specific

Please fill out the form completely. Print a copy and Refer to SOP instructions for assistance.	insert into your Safety on Site Binder.	
Department:	Date:	
Principal Investigator:		
Chemical Hygiene Officer:		
Laboratory Phone:	Office Phone:	
Emergency Contact:(Name and Phone Number)		
Location(s) covered by this SOP:		
1. Type of SOP (check one)		
Process Hazardous Chemical	Hazard Class	
2. Describe Process, Hazardous Chemical or Class:		
3. Potential Hazards:		

4. Circumstances Requiring Prior Approval:

- 5. Personal Protective Equipment (PPE):
- 6. Engineering Controls:
- 7. Special Handling & Storage Requirements:
- 8. Spill & Accident Procedures:
- 9. Decontamination Procedures:
- 10. Waste Disposal Procedures:
- 11. Designated Area:
- 12. Safety Data Sheet (SDS) Location:
- 13. Protocol(s):

Appendix E: Safe Use of Particularly Hazardous Substances^{*}

Safe Handling of Particularly Hazardous Substances Guidelines

I. REFERENCES

 Title 8, California Code of Regulations (CCR), Section 5191 (Occupational Exposures to Hazardous Chemicals in Laboratories; Article 110 (Regulated Carcinogens); Section 5209 (Listed Carcinogens); Section 5203 (Report of Use Requirements); Section 5154.1 (Ventilation Requirements for Laboratory-Type Hood Operations);

II. PURPOSE

To provide general guidance on how to work safely with chemicals that have been designated as "particularly hazardous" by Cal/OSHA. It describes the minimum requirements for the safe storage, use, handling, and disposal of particularly hazardous substances, including spill and accident response procedures. Particularly hazardous substances are defined by Cal/OSHA as: reproductive toxins, acutely toxic substances and select carcinogens, which include regulated carcinogens. Refer to Attachment A, Particularly Hazardous Substances Definitions, for specific definitions.

III. STATEMENT

These guidelines apply to all UCI laboratory workers (i.e., Principal Investigators, laboratory personnel, students, visiting researchers, etc.) who use or work with particularly hazardous substances. Careful handling and stringent controls of these chemicals are essential to protect workers and the environment, and to comply with Cal/OSHA regulations.

Additional safety requirements may apply, depending on the specific chemical. For example, carcinogens that are also highly flammable require both particularly hazardous substance controls as well as fire safety controls. Contact EH&S, 4-6200 for guidance on use of chemicals that may require further controls. Information and guidance on handling of particularly hazardous substances can also be found in UCI's Chemical Hygiene Plan.

IV. LABORATORY SAFETY REQUIREMENTS & PROCEDURES

A. Laboratory Specific Standard Operating Procedures

1. Individual laboratory groups must prepare and maintain laboratory-specific standard operating procedures (SOP) for identifying hazards and handling methods to avoid exposure to particularly hazardous substances. The procedures must indicate the designated use areas, limitations on the quantities and procedures used, information on containments, and information on hazards involved. These procedures may be specific to particular substances or generalized over a group of chemicals with similar hazardous properties and use limitations. Chemical-specific procedures must be developed for each Cal/OSHA regulated carcinogen and procedures should be developed for reproductive toxins, acutely toxic

materials, and select carcinogens. EH&S can provide additional guidance for specific chemical hazards.

- 2. A copy of the particularly hazardous substances procedures, including laboratory specific information, and the Safety Data Sheets (SDS) for the chemical(s) used must be readily accessible in the lab.
- 3 EH&S must be notified immediately if members of the laboratory become ill or exhibit signs or symptoms associated with exposure to hazardous chemicals used in the laboratory. Affected employees must be provided immediate first aid and medical surveillance within 24hours of the event.
- 4. Principal Investigators must identify what classes of particularly hazardous substances are in use in their labs and identify the appropriate personal protective equipment (PPE) on their Laboratory PPE Assessment Tool, which must be completed as conditions change in the laboratory, or at least once each calendar year.

B. Training and Documentation

- 1. All laboratory personnel who work with or may be exposed to particularly hazardous substances must be provided laboratory-specific training and information by the Principal Investigator or their designee prior to beginning their initial assignment. Laboratory-specific training should cover specific policies and procedures, etc. and is in addition to the basics covered in the Laboratory Safety training. Records of laboratory-specific training must be maintained in the laboratory and should include an outline of the topics covered. See http://www.ehs.uci.edu/programs/iipp/Work_Unit-Specific_Training_Roster.doc for a sample documentation form. Training shall include:
 - The hazards/toxicological effects associated with the chemicals being used.
 - Routine procedures and decontamination methods.
 - Emergency response practices and procedures.
 - Methods and observations for detecting the presence or release of hazardous chemicals.
 - Available protection measures, including appropriate work practices and personal protective equipment (PPE).
 - A review of written SOP and SDSs and the Chemical Hygiene Plan (CHP).
 - A review of these guidelines.
- 2. All laboratory personnel are responsible for knowing and complying with all safety guidelines, regulations, and procedures required for the task assigned and for reporting unsafe conditions, accidents or near misses to the Principal Investigator, immediate laboratory management staff or EH&S.
- Continuing training shall be conducted as needed to maintain a working knowledge of hazards and the safety requirements for all laboratory personnel who work with particularly hazardous substances. Written records must be maintained for each training session. See http://www.ehs.uci.edu/programs/iipp/Work_Unit-Specific_Training_Roster.doc for a sample documentation form.

C. Use in Designated Areas

1. Designated area(s) for use of particularly hazardous substances must be formally established by developing SOPs and posting appropriate signage. This designated area(s) may be an entire laboratory, a specific work bench, or a chemical fume hood. When particularly hazardous substances are in use, access to the designated area shall be limited

to personnel following appropriate procedures and who are trained in working with these chemicals.

- 2. Access to areas where particularly hazardous substances are used or stored must be controlled by trained employees. Working quantities of particularly hazardous substances should be kept as small as practical and their use should be physically contained as much as possible, usually within a laboratory fume hood or glove box. It is the responsibility of each Principal Investigator, or their designee, to train and authorize their staff for these operations and to maintain documentation of this training and authorization.
- 3. Signage is required for all containers, designated work areas and storage locations. Sign wording must state the following as appropriate for the specific chemical hazard:

"DANGER, CANCER HAZARD – SUSPECT AGENT" "DANGER, CANCER HAZARD – REGULATED CARCINOGEN" "DANGER, REPRODUCTIVE TOXIN" "DANGER, ACUTE TOXIN"

Entrances to designated work areas and storage locations must include signage, "AUTHORIZED PERSONNEL ONLY", in addition to the above specific hazard warning wording. Signage templates can be obtained from the UC Chemistry and Biochemistry safety webpage.

- 4. Work surfaces should be stainless steel, plastic trays, dry absorbent plastic backed paper, chemically resistant epoxy surfaces, or other chemically impervious material.
- 5. Protocols, procedures, and experiments must be designed and performed in a manner to safely maintain control of the particularly hazardous substances. Laboratory personnel must specifically consult with their Principal Investigators if a special hazard is involved (e.g., material under pressure) or if they are uncertain of the potential hazards.

D. Personal Protective Equipment (PPE)

- 1. PPE must be sufficient to protect eyes and skin from contact with the hazardous agents. At minimum, safety glasses, lab coat, long pants, closed toe shoes, and gloves are required when working with particularly hazardous substances. Visit http://www.ehs.uci.edu/PPE.html for more information. Goggles may be required for processes in which a splash or spray hazard may exist and flame resistant lab coats may be required if the chemicals being used are flammable.
- 2. Refer to the specific chemical's SDS and SOP for specific information on additional PPE and glove selection.
- 3. Contaminated PPE and clothing must be disposed of or decontaminated prior to removal from the designated work area. While small spots of contamination may be cleaned in the lab, grossly contaminated lab coats may need to be disposed of as dry hazardous waste. Refer to http://www.ehs.uci.edu/PPE.html and the Chemical Hygiene Plan for guidance on handling contaminated protective apparel and other PPE.

E. Engineering Controls

- 1. Bench top work with particularly hazardous substances should be avoided whenever practical in favor of contained systems (such as fume hoods or glove boxes) and is not permitted if there is a reasonable likelihood of workers exceeding regulatory exposure limits. For questions regarding exposure limits and for assistance in conducting a hazard assessment for uncontained procedures, contact EH&S, 4-6200.
- Laboratories and rooms where particularly hazardous substances are used outside of containment systems must have general room ventilation that is maintained at negative pressure with respect to public areas. Air from these ventilation systems must be vented externally; recirculation is not permitted. Doors providing access from public areas must be kept closed.

F. Special Handling & Storage Requirements

- 1. Particularly hazardous substances must be stored in a designated area and used in a manner that will minimize the risk of accidental release (e.g., capped tightly, use of chemical resistant secondary containment, whenever possible). Laboratory personnel should remove chemicals from storage only as needed and return them to storage as soon as practical.
- 2. Chemicals should be segregated from incompatible materials, as described in the UC Chemical Hygiene Plan. The use of particularly hazardous substances must be confined to an established designated area (see C. Use in Designated Areas, above).
- 3. Additional requirements for the safe storage of a specific chemical may be found in the manufacturer's instructions or in the SDS.
- 4. When transporting chemicals beyond the immediate laboratory environment, containers should be protected from breakage by using a bottle carrier or other effective containment.
- 5. Contact EH&S, 4-6200. for guidance on the planned use of chemicals that may require further controls.

G. Spill & Accident Procedures

- 1. Immediate measures must be available to prevent the possible spread of contamination in the event of a small spill of a particularly hazardous substance. Absorbent materials and clean up materials should be available in all laboratories sufficient to contain and decontaminate individuals and equipment and areas. Any known spills must be contained and decontaminated as soon as possible.
- 2. In the event of a large spill that is beyond a laboratory group's immediate response capabilities, the following procedures should be followed:
 - a. Evacuate the area immediately.
 - b. Restrict access to the affected areas to emergency responders and post signage and barriers as needed to prevent unauthorized entry.
 - c. Contact EH&S immediately for response. Call 911 from a UC campus phone or from a cell phone (to UCIPD).
- 3. In the event of direct skin contact with a particularly hazardous substance, the affected person must shower or flush the affected areas for a minimum of 15 minutes. Whenever personal contamination occurs, the event must be reported to EH&S, 4-6200 and an incident report will be completed and maintained by EH&S.

- 4. If the spill involves acutely toxic materials, the spill should be treated as a large spill if there is any doubt about the group's ability to safely mitigate the spill.
- 5. If the spill involves regulated carcinogens, a Report of Use may need to be filed (see J. Regulated Carcinogens and Report of Use Requirements, below).

H. Routine Decontamination Procedures

- 1. To limit the spread of contamination, laboratory work surfaces should be decontaminated at the conclusion of each procedure and at the end of each day on which particularly hazardous substances are used.
- 2. All equipment should be decontaminated before removing it from the designated area; this decontamination should be carried out in a glove box or fume hood where practical.
- 3. Contaminated PPE must not be removed from the designated area until properly decontaminated; refer to the Chemical Hygiene Plan for guidance on the cleaning of protective apparel and other PPE. After working with these chemicals, gloves must immediately be removed and disposed of as hazardous waste and hands and arms washed with soap and water.

I. Waste Disposal Procedures

- 1. Disposal of waste materials that include particularly hazardous substances must comply with the hazardous chemical waste disposal procedures found in the Laboratory Safety Manual.
- 2. In addition to general hazardous waste labeling requirements, waste containers containing particularly hazardous substances must also be labeled as appropriate for the specific chemical hazard:

"DANGER, CANCER HAZARD – SUSPECT AGENT"

"DANGER, CANCER HAZARD – REGULATED CARCINOGEN"

"DANGER, REPRODUCTIVE TOXIN"

"DANGER, ACUTE TOXIN"

Signage templates can be obtained from the UC Chemistry and Biochemistry safety webpage.

3. All non-radioactive chemical waste must be disposed of through the UCI Hazardous Waste Management Program. Due to regulatory restrictions and the high cost of disposal, the Radiation Safety Department should be contacted prior to producing mixed wastes of hazardous chemicals and radioactive material.

J. Regulated Carcinogens and Report of Use Requirements

 Regulated carcinogens are a specific subset of select carcinogens which have special additional requirements associated with their use under certain circumstances. See Attachment B for the specific list. EH&S maintains an air sampling program to monitor individuals to determine if they are, or may reasonably be expected to, exceed short or long term exposure limits. Every effort should be made to minimize exposure and keep exposure levels below these limits by using fume hoods, limiting the quantities used, and following SOP designed to reduce exposure. If levels cannot be kept below these levels, additional requirements may include:

- Required medical evaluations.
- Additional documented training.
- Use of respirators with required initial and ongoing training, medical evaluations, and maintenance documentation.
- Additional documented hazard evaluations.
- Listed carcinogens are a further subset of regulated carcinogens. See Attachment C for the specific list. The use of these materials must be registered with EH&S through the Laboratory PPE Hazard Assessment Tool or other equivalent EH&S approved process. An evaluation will be completed to assess safety requirements for groups that use these materials.

Report of Use Requirements must be met for each group when they:

- Begin the use of, or make significant changes to existing use of any listed carcinogen.
- Use regulated carcinogens such that there is a reasonable expectation that exposure limits may be exceeded.
- In the event of an emergency in which employees have been exposed to any regulated carcinogen.

V. ATTACHMENTS

- A. Particularly Hazardous Substances Definitions
- B. Regulated Carcinogens
- C. Listed Carcinogens

ATTACHMENT A

Particularly Hazardous Substances Definitions

Particularly hazardous substances fall into the following three major categories: acute toxins, reproductive toxins, and carcinogens.

Section 1.01 Acute Toxins

Substances that have a high degree of acute toxicity are substances that may be fatal or cause damage to target organs as the result of a single exposure or exposures of short duration. They can be defined as:

- 1. A chemical with a median lethal dose (LD50) of 50 mg or less per Kg of body weight when administered orally to albino rats weighing between 200 and 300 gm each;
- 2. A chemical with a median lethal dose (LD50) of 200 mg or less per Kg of body weight when administered by continuous contact for 24 hours (or less if death occurs within 24 hours) with the bare skin of albino rabbits weighing between 2 and 3 Kg each; and
- 3. A chemical that has a median lethal concentration (LC50) in air of 5000 ppm by volume or less of gas or vapor, or 50 mg per liter or less of mist, fume, or dust, when administered by continuous inhalation for 1 hour (or less if death occurs within 1 hour) to albino rats weighing between 200 and 300 gm each.

Section 1.02 Reproductive Toxins

Reproductive toxins include any chemical that may affect the reproductive capabilities including chromosomal damage (mutations) and effects on fetuses (teratogenesis). A list of reproductive toxins is maintained online at http://www.oehha.ca.gov/prop65/prop65_list/Newlist.html#files.

Section 1.03 Carcinogens

Carcinogens are chemical or physical agents that cause cancer. Generally, they are chronically toxic substances; that is, they cause damage after repeated or long-duration exposure, and their effects may only become evident after a long latency period.

The term "regulated carcinogen" means a recognized cancer causing substance, compound, mixture, or product regulated by Cal/OSHA sections 1529, 1532, 1532.2, 1535, 8358, 8359 or Article 110, sections 5200-5220. See Attachment B for the specific list of Regulated Carcinogens.

The term "Listed Carcinogen" refers to a specific list of 13 chemicals regulated by Cal/OSHA and Federal OSHA and has specific use and handling requirements. See Attachment C for the specific list of Listed Carcinogens.

The term "select carcinogen" refers to a category of chemicals where the available evidence strongly indicates that the substances cause human carcinogenicity. A select carcinogen meets one of the following criteria:

- 1. It is regulated by Cal/OSHA as a carcinogen; or
- 2. It is listed under the category "known to be carcinogens" in the annual report by the National Toxicology Program (NTP); or
- 3. It is listed under Group 1 "carcinogenic to humans" by the International Agency for Research on Cancer (IARC); or

- 4. It is listed in either Group 2A or Group 2B by the IARC or under the category "reasonably anticipated to be carcinogens" by the NTP, and causes statistically significant tumor incidence in experimental animals in accordance with any of the following criteria:
 - a. 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;

- b. After repeated skin application of less than 300 mg/kg of body weight per week; or
- c. After oral dosages of less than 50 mg/kg of body weight per day.

ATTACHMENT B

Regulated Carcinogens

The term "regulated carcinogen" means a recognized cancer causing substance, compound, mixture, or product regulated by Cal/OSHA sections 1529, 1532, 1532.2, 1535, 8358, 8359 or Article 110, sections 5200-5220.

- Acrylonitrile
- Arsenic metal and inorganic arsenic compounds
- Asbestos
- Benzene
- 1,3-butadiene
- Cadmium metal and cadmium compounds
- Chromium(VI) compounds
- Coke Oven Emissions
- 1,2-Dibromo-3-chloropropane (DBCP)
- Ethylene Dibromide (EDB)
- Ethylene Oxide (EtO)
- Formaldehyde gas and formaldehyde solutions
- Lead metal and inorganic lead compounds
- Methylene Chloride
- 4,4'-Methylene bis(2-chloroaniline) (MBOCA)
- Methylenedianiline (MDA)
- Vinyl Chloride
- 2-Acetylaminofluorene
- 4-Aminodiphenyl
- Benzidine (and its salts)
- 3,3'-Dichlorobenzidine(and its salts)
- 4-Dimethylaminoazobenzene
- alpha-Naphthylamine
- beta-Naphthylamine
- 4-Nitrobiphenyl
- N-Nitrosodimethylamine
- beta-Propiolactone
- bis-Chloromethyl ether
- Methyl chloromethyl ether
- Ethyleneimine

ATTACHMENT C

Listed Carcinogens

The term "listed carcinogen" refers to a specific list of 13 chemicals regulated by Cal/OSHA and Federal OSHA and has specific use and handling requirements.

- 2-Acetylaminofluorene
- 4-Aminodiphenyl
- Benzidine (and its salts)
- 3,3'-Dichlorobenzidine(and its salts)
- 4-Dimethylaminoazobenzene
- alpha-Naphthylamine
- beta-Naphthylamine
- 4-Nitrobiphenyl
- N-Nitrosodimethylamine
- beta-Propiolactone
- bis-Chloromethyl ether
- Methyl chloromethyl ether
- Ethyleneimine

Appendix F: Regulated Carcinogens

Cal/OSHA Regulated Carcinogens fall into a higher hazard class and have extensive additional requirements associated with them. The use of these agents may require personal exposure sampling based on usage. The following is the list of Cal/OSHA Regulated Carcinogens.

Cal/OSHA Regulated Carcinog	ens	
Acrylonitrile	Arsenic (Inorganic)	Ethylene Oxide (EtO)
(MBOCA)	Asbestos	Ethyleneimine
1,2-Dibromo-3-chloropropane		
(DBCP)	Benzene	Formaldehyde
1,3-butadiene	Benzidine (and its salts)	Lead
2-Acetylaminofluorene	Beta-Naphthylamine	Methyl chloromethyl ether
3,3'-Dichlorobenzidine(and its	Beta-Propiolactone	
salts)		Methylene Chloride
4,4'-Methylene bis(2-chloroaniline)	Bis-Chloromethyl ether	Methylenedianiline (MDA)
4-Aminodipheny	Cadmium	N-Nitrosodimethylamine
4-Dimethylaminoazobenzene		Non Asbestiform Tremolite,
	Chromium (VI)	Anthophyllite, and Actinolite
4-Nitrobiphenyl	Coke Oven Emissions	Vinyl Chloride
Alpha-Naphthylamine	Ethylene Dibromide (EDB)	

Appendix G: Respiratory Hazard Assessment Form

(Part 1 To be completed by Employee)

UCI EH&S Respiratory Hazard Evaluation Part 1

Job Title:				Date:	
Department:					
Supervisor Name:			Phone Extension:		Email:
Employees Represented	by Evaluation:				
Name	UCI Net ID		Name		UCI Net ID
Process Description:					
Identity of Contaminant(s)/Hazard(s)?	cont	ntity of aminant used unit time:	uration	of Exposure:
Controls and/or persona	I protective equipme	ent be	ing used to minin	nize or e	liminate exposure?
Expected physical work effort:	🗖 High		□ Moderate		🗖 Low

Physical Work Effort Key (based on ACGIH TLV and BEI handbook)

High: Examples of activities are sawing by hand, shoveling dry/wet sand, intermittent heavy lifting with pushing or pulling

Moderate: Examples of activities are scrubbing in standing position, walking about with moderate lifting or pushing

Low: Examples of activities are sitting with moderate arm and leg movements, standing with light work at machine or bench while using mostly arms or with some walking about

Obtain this form online at: http://www.ehs.uci.edu/programs/ih/respiratory.html

(Part 2 To be completed by EH&S)

UCI EH&S Respiratory Hazard Evaluation Part 2

Evaluation By:		Revi	ewed B	y:			□ New	Revised	
	What type of respiratory hazard is D				□ Oxygen □ Gas/ □ Part Deficiency Vapor Aeroso				
present?		🗖 Con	nbinatior	n	🗖 Bioha	azard			
Respiratory Hazard(s)			ΓLV? ¹	ST	EL/PEL? ¹	Conc	entration in the	atmosphere? ²	
1 Mark "NONE" if value is n 2 Provide reasonable estin		data is i	not availa	able					
Relative Humidity: (report					erature: (<i>r</i> e	eport po	tential range)	
Are IDLH conditions possi					eye irritant		□ No □ Ye	6	
Are engineering controls available?	□ No □ Yes		ls haza skin?	ard abso	orbed thro	ugh the	□ No □ Ye	3	
Is a respirator required?	□ No □ Yes (Based on Check all that apply:				 (Refer to Appendix B- Respirator Decision Logic Sequence) Full Face Air line Filtering Facepiece 				
Cartridge type(s) to be issu (Refer to Appendix B- Respirator D Recommended Change So	Decision Logic Sequ	kimate v lence)	J. J	·		0 ()		every 3 hours)	
Additional required and/or	recommended	P.P.E.	(person	al prote	ective equi	pment)			
Expected duration and free	quency of respi	irator us	se:					-	
Comments/Notes:									

Appendix H: Peroxide Forming Chemicals Common to Research

Class 1 PFCs

Class 1 chemicals form peroxides after prolonged storage. The chemicals listed below should be <u>tested for the formation of peroxides on a periodic basis</u>. Several methods are available to check for peroxides; the two most common are the use of peroxide test strips or the potassium iodide test.

Class 1 PFCs		
Isopropyl ether	Potassium amide	Vinylidene chloride
Divinyl acetylene	Potassium metal	
Divinyl ether	Sodium amide	

Class 2 PFCs

This group of chemicals will readily form peroxides when they become concentrated (e.g., via evaporation or distillation). The concentration process defeats the action of most auto-oxidation inhibitors. As a result, these chemicals should be <u>disposed of within12 months of receiving</u>.

Class 2 PFCs		
Acetal	Diethylether	Methyl isobutyl ketone
Cumene	Dioxane	Tetrahydrofuran
Cyclohexene	Ethylene glycol dimethyl ether	Tetrahydronaphthalene
Cyclopentene	Furan	Vinyl ethers
Diacetylene	Methylacetylene	
Dicyclopentadiene	Methylcyclopentane	

Class 3 PFCs

This group of chemicals forms peroxides due to initiation of polymerization. When stored in a liquid state, the peroxide forming potential dramatically increases. These chemicals should be disposed of <u>if they become degraded or are no longer needed</u>.

Class 3 PFCs		
Acrylic acid	Chlorotrifluoroethylene	Vinyl acetate
Acrylonitrile	Methyl methacrylate	Vinyl acetylene Vinyl chloride
Butadiene	Styrene	Vinyl pyridine
Chlorobutadiene	Tetrafluoroethylene	Vinylidene chloride

Appendix I: Safe Use of Pyrophoric Reagents

Procedures for Safe Use of Pyrophoric Reagents

I. Introduction

In December 2008, a laboratory accident at UCLA occurred while the researcher was working with t-butyl lithium, a highly pyrophoric agent. Pyrophoric materials ignite spontaneously on contact with air; these chemicals react with oxygen, moisture in the air, or both. Failure to follow proper handling procedures can result in fire or explosion, leading to serious injuries/death or significant damage to facilities. Good technical guidance can be found in **Aldrich Technical Bulletins AL-134 and AL-164** (http://www.sigmaaldrich.com/chemistry/aldrich-chemistry/tech-bulletins.html)

Below are some procedures describing the hazards, proper handling, disposal and emergency procedures when working with pyrophoric materials.

II. Examples of Pyrophoric Materials

Grignard Reagents: RMgX (R=alkyl, X=halogen) Metal alkyls and aryls: Alkyl lithium compounds; tert-butyl lithium Metal carbonyls: Lithium carbonyl, nickel tetracarbonyl Metal powders (finely divided): Cobalt, iron, zinc, zirconium Metal hydrides: Sodium hydride Nonmetal hydrides: Diethylarsine, diethylphosphine Non-metal alkyls: R₃B, R₃P, R₃As; tetramethyl silane, tributyl phosphine Phosphorus Potassium Sodium Gases: Silane, dichlorosilane, diborane, phosphine, arsine

A more extensive list of pyrophoric compounds can be found in Bretherick's *Handbook* of *Reactive Chemical Hazards*

III. Hazards

Pyrophorics must be handled under inert atmospheres and in such a way that rigorously excludes air/moisture since they ignite on contact with air and/or water. They all tend to be toxic and many come dissolved in a flammable solvent. Other common hazards include corrosivity, teratogenicity, water reactivity, peroxide formation, along with damage to the liver, kidneys, and central nervous system. Be especially vigilant when working tertiary butyl lithium which is **extremely pyrophoric.** Researchers working with pyrophoric materials must be proficient and must not work alone!

IV. Controlling the Hazards

BEFORE working with pyrophoric reagents, users must:

1. Consult with your PI and confirm that approval has been received when working with highly hazardous materials.

- 2. Read the relevant Safety Data Sheets (SDS), technical bulletins, and guidance documents to understand and how to mitigate the hazards. The SDS must be reviewed before using an unfamiliar chemical and periodically as a reminder.
- 3. Prepare a written Standard Operating Procedure (SOP) identifying the safety precautions specific to the operations (<u>http://www.ehs.uci.edu/labres.html</u>)
 - Consider performing a "dry run" to identify and resolve possible hazards before conducting the actual procedure.
 - Users of pyrophoric materials must be trained in proper lab technique and be able to demonstrate proficiency.
 - Use less toxic or hazardous substances in your experiment and minimize the amount of hazardous waste generated.
- 4. Perform a hazard analysis and identify the failure modes in your experiment. Be prepared to handle accidents.
- 5. Know the location of eyewash/ shower, fire extinguishers, fire alarm pulls, and emergency exits.
- 6. Complete required EH&S safety training requirements (http://www.uclc.uci.edu/) and lab specific training. Address all Safety on site (SOS) issues.
- 7. Use the buddy system. Do not work alone or off hours where there are few people around to help
- 8. Wear the appropriate personal protective equipment.
 - Use a lab coat, goggles/face shield and gloves.
- 9. Maintain good work practices.
 - keep combustible materials, including paper towels and Kimwipes, away from pyrophoric reagents.
 - minimize the quantity of pyrophoric reagents used and stored and use the smallest quantity of material practical. It is better to do multiple transfers of small volumes than attempt to handle larger quantities. Consider using the cannula method when transferring more than 20 ml.
 - remove all excess and nonessential chemicals and equipment from the fume hood or glove box where pyrophoric chemicals will be used to minimize the risk of fire.
 - designate a fume hood or glove box for hazardous work.

A. Personal Protective Equipment (PPE)

Eye Protection

- Chemical splash goggles or safety glasses that meet the ANSI Z.87.1 1989 standard must be worn whenever handling pyrophoric chemicals. Ordinary prescription eye glasses will NOT provide adequate protection unless they also meet this standard. When there is the potential for splashes, goggles must be worn, and when appropriate, a face shield added.
- A face shield, worn over safety eyewear, is required any time there is a risk of explosion, large splash hazard or a highly exothermic reaction. All manipulations of pyrophoric chemicals which pose this risk should occur in a fume hood with the sash in the lowest feasible position. Portable shields, clamped to the counter top, may be used if fume hood space is not available.

Skin Protection

 Gloves must be worn when handling pyrophoric chemicals. Nomex pilot gloves should be used for handling these chemicals. Be sure to use adequate protection to prevent skin exposures. Sigma-Aldrich recommends the use of nitrile gloves underneath neoprene glovesⁱ.

- A lab coat made from Nomex is recommended for labs using these reagents routinely. Lab coats need to be buttoned and fit properly to cover as much skin as possible.
- Appropriate shoes, that cover the entire foot (closed toe, closed heel, no holes in the top) must be worn.

B. Safety Equipment

Have the proper equipment and the emergency phone number (9-1-1) readily available for any emergencies. The recommended fire extinguisher is a standard dry powder (ABC) type.

DO NOT use a carbon dioxide fire extinguisher or water to attempt to extinguish a pyrophoric material fire as these types of extinguishers can actually enhance the combustion of some pyrophoric materials. A small beaker of dry sand or soda ash (lime) in the work area is useful to extinguish any small fire that occurs at the syringe tip and to receive any last drops of reagent from the syringe.

Eyewash/ Safety Shower

• A combination eyewash/safety shower should be within 10 seconds travel time where pyrophoric chemicals are used. Inside the laboratory is optimum. Bottle type eyewash stations are not acceptable.

Fume Hood

• Verify that your fume hood has been checked in the last 12 months. Many pyrophoric chemicals release noxious or flammable gases, and some pyrophoric materials are stored under kerosene. These materials must be handled in a laboratory hood.

Glove (dry) box

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

Gas Cabinets

- Storage of pyrophoric gases is described in the California Fire Code, Chapter 41. Gas cabinets, with appropriate remote sensors and fire suppression equipment, are required.
- Gas flow, purge and exhaust systems should have redundant controls to prevent pyrophoric gas from igniting or exploding. All pyrophoric gases must have Restricted Flow Orifices (RFO) installed on the cylinder. Contact your gas supplier for assistance.
- Emergency back-up power should be provided for all electrical controls, alarms and safeguards associated with the pyrophoric gas storage and process systems.

V. Storage and Disposal

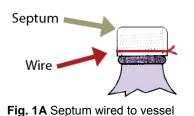
Storage

Some Pyrophoric materials cannot be stored in unsprinklered buildings; check list of restricted chemicals at:

http://www.ehs.uci.edu/programs/fire/ChemicalsNotPermittedInUnsprinkleredBuildings.pdf

- Use and store minimal amounts of pyrophoric chemicals.
- Do not store pyrophoric chemicals with flammable materials or in a flammable liquids storage cabinet. Containers carrying pyrophoric materials must be clearly labeled with the correct chemical name, in English, and hazard warning.
- Store as recommended in the SDS. A nitrogen-filled desiccator or glove box are suitable storage locations.
- If pyrophoric reagents are received in a specially designed shipping, storage or dispensing container, (such as the Aldrich Sure/Seal packaging system) ensure that the integrity of that container is maintained.
- Ensure that sufficient protective solvent, oil, kerosene, or inert gas remains in the container while the material is stored.
- NEVER return excess chemical to the original container. Small amounts of impurities introduced into the container may cause a fire or explosion.
- For storage of excess chemical, prepare a storage vessel in the following manner:
 - Select a septum that fits snugly into the neck of the vessel
 - Dry any new empty containers thoroughly
 - Insert septum into neck in a way that prevents atmosphere from entering the clean dry (or reagent filled) flask.
 - Insert a needle to vent the flask and quickly inject inert gas through a second needle to maintain a blanket of dry inert gas above the reactive reagent.
 - Once the vessel is fully purged with inert gas, remove the vent needle then the gas line.

For long-term storage, the septum should be secured with a



 For extra protection a second same-sized septa (sans holes) can be placed over the first (figure 1b).

copper wire (figure 1A).

• Use parafilm around the outer

septa and (obviously) remove the parafilm and outer septum before accessing the reagent through the primary septum³.

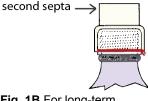


Fig. 1B For long-term storage, use a second septum



Disposal of Pyrophoric Reagents

- A container with any residue of pyrophoric materials should never be left open to the atmosphere.
- Any unused or unwanted pyrophoric materials must be destroyed by transferring the materials to an appropriate reaction flask for hydrolysis and/or neutralization with adequate cooling⁴.

- The essentially empty container should be rinsed three times with an inert dry solvent; this rinse solvent must also be neutralized or hydrolyzed. The rinse solvent must be added to and removed from the container under an inert atmosphere.
- After the container is triple-rinsed, it should be left open in back of a hood or ambient atmosphere at a safe location for at least a week. After the week, the container should then be triple rinsed again.
- The empty container, solvent rinses and water rinse should be disposed as hazardous waste.

Disposal of Pyrophoric Contaminated Materials

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

Important Steps to Follow

Pyrophoric reagents can be handled and stored safely as long as all exposure to atmospheric oxygen and moisture is avoided. Finely divided solids must be transferred under an inert atmosphere in a glove box. Liquids may be safely transferred without the use of a glove box by employing techniques and equipment discussed in the Aldrich Technical Information Bulletin AL-134. Pyrophoric gases should be handled in compliance with the California Fire Code, Chapter 41.

Handling Pyrophoric Liquids

- Users should read and understand the Aldrich Technical Information Bulletin No. AL-134. The PI should also have in place laboratory-specific handling, storage, and disposal standard operating procedures. The standard operating procedures should be included in the lab Chemical Hygiene Plan.
- By using proper syringe techniques, these reagents can be handled safely in the laboratory. The Aldrich Sure/Seal[™] Packaging System provides a convenient method for storing and dispensing air-sensitive reagents.
- The reagent can be dispensed using a syringe or double-tipped needle (16, 18 or 20 gauge) inserted through the hole in the metal cap, as shown in fig. 2 below. It is recommended that the plastic cap be replaced after each use and in particular for long-term storage.

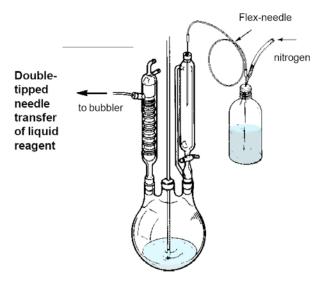


Fig. 2 Double-tipped needle transfer of liquid reagent

• For extended storage of unused reagents, use the solid plastic cap, or equip the bottle with an Oxford Sure/Seal valve cap, or transfer the reagent to a suitable storage vessel, as described above.

Emergency Procedures

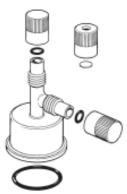
Spill

- Powdered lime should be used to completely smother and cover any spill that occurs.
- DO NOT use water to attempt to extinguish a pyrophoric material fire as it can actually enhance the combustion of some pyrophoric materials, e.g. metal compounds.
- Do not use combustible materials (paper towels) to clean up a spill, as these may increase the risk of igniting the pyrophoric compound. Soda ash (powdered lime) or dry sand should be used to completely smother and cover any small spill that occurs.
- A container of powdered lime should be kept within arm's length when working with a pyrophoric material.
- If anyone is exposed, or on fire, wash body with copious amounts of water.
- The recommended fire extinguisher is a standard dry powder (ABC) type. Class D extinguishers are recommended for combustible solid metal fires (e.g, sodium, LAH), but not for organolithium reagents.
- Call 9-1-1 for emergency assistance

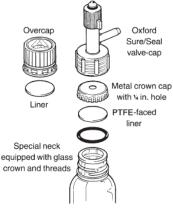
Excerpt from the Sigma-Aldrich Technical Bulletins AL-134 and AL-164 at: <u>http://www.sigmaaldrich.com/chemistry/aldrich-chemistry/tech-bulletins/tech-bulletin-numbers.html</u>

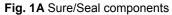
The Aldrich^{ⁱⁱ} Sure/Seal[™] Packaging System

The Sure/Seal packaging system (**Fig. 1A**) provides a convenient method for storing and dispensing air-sensitive reagents. The reagent can be dispensed using a syringe or double-tipped needle (16, 18 or 20 gauge) inserted through the hole in the metal cap. When inserting a needle through a septum, a layer of silicone or hydrocarbon grease on the septum



will help. Upon withdrawal of the needle, the small hole that remains in the PTFE liner will not cause the reagent to deteriorate under normal circumstances. However, it is recommended that the plastic cap be replaced after each use and in particular for long-term storage.





For extended storage of unused reagents, use the solid plastic cap, or equip the bottle with an Oxford Sure/Seal valve cap, or transfer the reagent to a suitable storage vessel.

Fig. 1B Sure/Seal septum-inlet transfer adapter

The Sure/Seal septum-inlet transfer adapter (**Fig. 1B**) can be used when repeated dispensing is necessary. The adapter protects the

contents of the bottles from air and moisture.

Transferring Pyrophoric Reagents with Syringe

- In a fume hood or glove box, clamp the reagent bottle to prevent it from moving
- Clamp/secure the receiving vessel too.
- After flushing the syringe with inert gas, depress the plunger and insert the syringe into the Sure/Seal bottle with the tip of the needle below the level of the liquid
- below the level of the liquid
 Secure the syringe so if the plunger blows out of the body it, and the contents will not impact anyons (cim it)

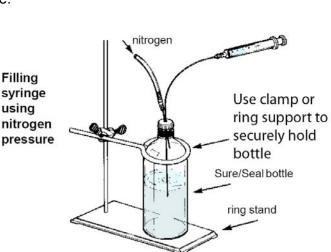
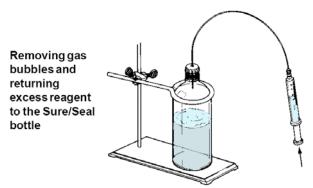


Fig. 2A Filling syringe using nitrogen pressure

- contents will not impact anyone (aim it toward the back of the containment)
- Insert a needle from an inert gas source carefully keeping the tip of the needle above the level of the liquid
- Gently open the inert gas flow control valve to slowly add nitrogen gas into the Sure/Seal bottle.
- This will allow the liquid to slowly fill the syringe (up to 100mL) as shown in **Fig. 2A**. Pulling the plunger causes gas bubbles.

- Let nitrogen pressure push the plunger to reduce bubbles. Excess reagent and entrained bubbles are then forced back into the reagent bottle as shown in Fig. 2B.
- The desired volume of reagent in the syringe is quickly transferred to the reaction apparatus by puncturing a rubber septum as illustrated in **Fig. 2C**.



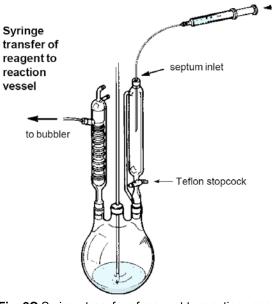


Fig. 2B Removing gas bubbles and returning excess reagent to the Sure/Seal bottle

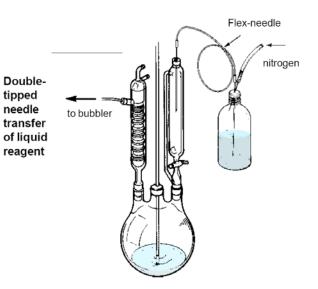
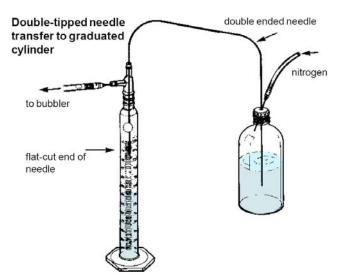


Fig. 2C Syringe transfer of reagent to reaction vessel

Transferring Pyrophoric Reagents with a Double-Tipped Needle (Cannula)



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



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

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

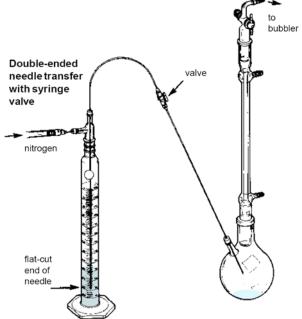


Fig. 3C Double-ended needle transfer with syringe valve

¹ Created from a variety of resources, principally the Sigma-Aldrich Technical Bulletins AL-134 and AL-164 at: http://www.sigmaaldrich.com/chemistry/aldrich-chemistry/tech-bulletins/tech-bulletinnumbers.html

¹Private communication to Rebecca Lally (rrlally@uci.edu) at UC Irvine in January 2009

¹ Images and advice from Sigma-Aldrich Technical Bulletins

⁴ Destruction of Hazardous Chemicals in the Laboratory ,George Lunn, Eric B. Sansone ,Wiley-Interscience; 2nd edition (March 1994) , ISBN: 047157399X

Additional References:

Leonard J., B. Lygo, and G. Procter, Advanced practical organic chemistry. London : Blackie ; New York : Chapman and Hall, 1995, pages 76-98.

Prudent Practices in the Laboratory: Handling and Disposal of Chemicals , National Research Council Publisher: National Academies Press; 1 edition (January 10, 2000), ISBN: 0309052297

We wish to acknowledge the following sources: Brandeis University, Standard Operating Procedure for Pyorphoric Chemicals; University of Nebraska, Lincoln, Pyrophoric Chemicals Standard Operating Procedure; University of Pittsburgh Safety Manual, Flammable and Pyrophoric Gas; Rochester University, SOP for Pyrophoric Chemicals.

Personal communication with(and grateful acknowledgement to) Dr. Russell Vernon, Environmental Health and Safety, UC, Riverside; Dr. Joseph Pickel, Center for Nanophase Materials Sciences, Oak

Ridge National Laboratory; Dr. Neal Langerman, Principal, Advanced Chemical Safety, Inc.; Dr. Frank Osterloh, Professor of Chemistry, UC Davis.

Grateful acknowledgement to Russell Vernon (russell.vernon@ucr.edu), Debbie Decker, (dmdecker@ucdavis.edu) and the UC Lab Safety Workgroup.

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View online at EH&S website: Pyrophoric Reagent (SOP) and Pyrophoric Safety (Video) .

Appendix J: Work Unit-Specific Training Roster

Work Unit-Specific Training Documentation (retain in SOS binder)

Topic(s) Covered: _____

Trainer: _____ Signature: _____

Date of Training: _____

Trainee Name	Trainee Signature	Date
-		
1		
<u> </u>		1

Obtain this form on the EH&S website at http://www.ehs.uci.edu/programs/iipp/Work_Unit-Specific_Training_Roster.doc

Appendix K: Laboratory Inspection Checklist

UNIVERSITY OF CALIFORNIA, IRVINE, ENVIRONMENTAL HEALTH AND SAFETY Laboratory Safety Survey

Section A - Lab Area Summary (please complete any missing information)					
Date:	Assigned Surveyor:				
PI Name: Phone:					
Lab Contact Name: Phone:					
Department: Dept Admin:					
Last survey date:					
Location:					
Please note any changes to the rooms in	cluded in this survey:				

ltem#	Lab or Research Characteristics	YES	NO	Room(s) where applicable	Notes	Instructions/email
1	Local Exhaust other than fume hoods present (circle) (e.g. snorkel, slothood, necropsy, toxic gas cabinet, ductless chemical hood)					Type/location to asamala@uci.edu
2	Chemical fume hoods have in-tact green EH&S sticker					Location to asamala@uci.edu
3	Lab uses or fabricates nanomaterials					PI/location to rrlally@uci.edu
4	Toxic gases present (DOT Division 2.3) Types:					PI/Type rrlally@uci.edu
5	Does lab engage in any outside field work?					PI/description to
6	Other unusual hazards associated with lab area or research					

Please answer every question by checking Yes or No, circling where appropriate and noting specific locations.

Lab Representative's Acknowledgement of Receipt of LAB SAFETY SURVEY COURTESY NOTICE - Items require require immediate action within 2 business days.

Print Na	me	Signature	Date
LABORA	ATORY SAFETY SURVEY-SECTION B		
		Y N NA Last Survey/ROOM(S)	InstructionsComments
Administ	trative		
1 (SI1)	Has work unit completed four (4) SOS milestones? Designation of SR; Safety Training Self-Assessments; Transcripts for Required EH Trainings; Documented Work Unit Specific Training		RE Training: Check for Lab Core Safety completion
2 (SI2)	Is required signage present and accurate? (PPI signage, ENI, Emergency Flipchart, Injuries and	E	Post current versions of appropriate

	Medical Treatment, appropriate Hazcom sign/ labels (BSL2, Biohazard, Rad, Carcinogens, and etc.)					signage
		Y	Ν	NA	Last Survey/ROOM(S)	InstructionsComments
Physical E	Environment				-	
3 (SI3)	Are tippable items >42 inches high seismically secured?					
4 (SI4)	Are heavy/hard items secured/limited in height?					
5 (SI5)	Are cabinet doors secured?					
6 (SI6)	Are storage shelves provided with lips or are cords taut?					
7 (SI7)	Is storage kept at least 18 inches below sprinkler heads and ceiling throughout room or area?					
8 (SI8)	Are aisles clear and unobstructed (36 inches lab aisles, 44 inches main aisles)?					
9 (SI9)	Is housekeeping up-to-standards? (trip hazards,spilled chemicals (residuals), paper clutter, and etc.)					Note specific issues in comments Provide Urgent Item notice.
10 (SI10)	Is floor in good repair to allow adequate cleaning?					
11 (SI11)	Are chairs and other furniture used in laboratory work covered with a non-fabric material that is easily decontaminated?					
12 (SI12)	Are ceiling tiles/panels in reasonable condition (not substantially damaged, moldy, or missing)?					
13 (SI13)	Is lab under negative pressure relative to corridor?					
		Y	Ν	NA	Last Survey/ROOM(S)	InstructionsComments
Fire/Life S	Safety					
14 (SI14)	Does staff know evacuation assembly location?					If not, point out Emergency Procedures poster location immediately; advertise Volunteer Opps!
15 (SI15)	Does staff know how to respond to emergencies?					If not review Flipchart Tabs
16 (SI16)	Does staff know where 1st Aid supplies are located?					
17 (SI17)	Are exit corridors and doors free from obstruction created by improper storage or arrangement of furniture?					Note specific issues in comments Provide Urgent Item notice.
18 (SI18)	Do fire doors and doors to hazardous areas self- close and latch properly?					
19 (SI19)	Are fire extinguishers provided within 50 feet of the lab, fully charged, pin and tamper ring in place, and up-to-date maintenance tag?					
20 (SI20)	Are trash receptacles and paper located away heat or arcing sources?					
21 (SI21)	Are fire alarm bells/horns/strobes free of obstruction that would hamper the operation or reduce the sound?					
22 (SI22)	Is emergency equipment (ie:, safety showers, fire alarm pull stations and fire extinguishers) physically and visually accessible?					Note specific issues in comments Provide Urgent Item notice.

Electrical/Mechanical Safety 24 (Si24) Are electrical cords and plugs in good repair, not cracked, broken, or frayed? Note specific issue: comments Provide Urgent Item notice. 25 (Si25) Are wall receptacles in good repair (not broken, covers in place, etc.)? Note specific issue: comments Provide Urgent Item notice. 26 (Si26) Is the area free of multi-plug (gang-plug) adapters? Image: covers in place, etc.)? Image: covers in place, etc.)? 27 (Si27) Are there fixed or portable GFCI devices used in area free of multi-plug (gang-plug) adapters? Image: covers in place, etc.)? Image: covers in place, etc.)? 28 (Si28) area free of multi-plug (gang-plug) adapters? Image: covers in place, etc.)? Image: covers in place, etc.)? Image: covers in place, etc.)? 28 (Si28) area thar are frequently wet (within 6 t. of a water source)? Image: covers in place, etc.)? Image: covers in place, etc.)? 29 (Si29) epites, pulleys, sprockets and chains, shafting, or other rotating parts of mechanical equipment property guarded (guard openings must be less than 1/2inch)? Image: covers in place, etc.)?	23 (S23)	Are refrigerators used appropriate for the location and items stored? (No domestics in lab outside of Clean Area, FMS for flammables)					
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39 (3139) Are non-bionazaruous sharp items, (broken giass)	39 (SI39)	Are non-biohazardous sharp items, (broken glass					

	and pointed plastic items) disposed of in a broken glass container?					
		Y	Ν	NA	Last Survey/ROOM(S)	InstructionsComments
Select Ag	ents and Controlled Substances					
40 (SI40)	Are inventory & usage log maintained?(CS / SA)					
41 (SI41)	Is there adequate storage security? (CS / SA)					
42 (SI42)	Are CS /SA disposed of in accordance with UCI procedures? (CS / SA)					
		Y	Ν	NA	Last Survey/ROOM(S)	InstructionsComments
Chemical	Safety					
43 (SI43)	Is lab staff keeping chemical inventories current within campus guidelines?					Verify and note last Inventory Date:
44 (SI44)	Does staff know how to access the campus Chemical Hygiene Plan? (Some work units fall under Haz Comm Std like Willed Body Program)					If no, show immediately.
45 (SI45)	Are hazardous chemical container labels readable with regard to chemical name and hazards?					
46 (SI46)	Are chemical containers in good condition (no leaking, cracked caps, rusting, crystals around neck)?					Note specific issues in comments Provide Urgent Item notice.
47 (SI47)	Are chemical containers kept securely closed when not in active use?					
48 (SI48)	Are containers of liquid hazardous chemicals over 1 gallon capacity stored below 5 feet high?					
49 (SI49)	For Peroxide forming chemicals: Is open-date noted?					
50 (SI50)	Is the operation of eyewash/safety showers checked monthly? (At UCIMC bar-code system; confirm that staff observe testing).					
51 (SI51)	Are flammable liquid materials stored according to UC Irvine guidelines?					
52 (SI52)	Are flammables materials stored away from heat and arc-sources?					Note specific issues in comments Provide Urgent Item notice.
53 (SI53)	Are incompatible chemical/wastes separated by distance or partition?					
54 (SI54)	Are corrosive liquids, including wastes, stored below shoulder level?					
55 (SI55)	Are employees instructed in incidental spill response?					
56 (SI56)	Do centrifuges have covers that are utilized during use?					
57 (SI57)	Is lab using fume hood correctly e.g. clear of obstructions and equipment; work contained past the front of the hood by 6 inches; sash position does not exceed approved working height / down when not in use.					
58 (SI58)	Are lab-specific SOPs for Particularly Hazardous Substances available (take printout from CIBRTRAC)?					
		Y	Ν	NA	Last Survey/ROOM(S)	InstructionsComments
Hazardou	s Chemical Waste					
59 (SI59)	Are wastes appropriately labeled?					

60 (SI60)	Are wastes in secondary containment?					
61 (SI61)	Are wastes sent to EH&S within 6 months?	ĥ	\square			
	·	Y	Ν	NA	Last Survey/ROOM(S)	InstructionsComments
Personal	Protective Equipment (PPE) and Hygiene					
62 (SI62)	Is PPE provided (may include safety glasses, goggles, gloves, aprons, faceshields)?					
63 (SI63)	Do lab workers wear closed-toed shoes and lab coats?					
64 (SI64)	Is PPE stored in a clean and sanitary location?					
65 (SI65)	Is staff conscientious removing PPE prior to exiting lab, handling telephones, etc?					
66 (SI66)	Have respirator/dust mask users been evaluated by EHS for respirator use?					
67 (SI67)	Is eating, drinking, and cosmetic use occurring only in areas signed as ?Clean Areas? and adequately separated from hazardous materials use and storage?					
68 (SI68)	Are refrigerators, microwaves and freezers labeled regarding the storage of hazardous materials or food items?					
		Y	Ν	NA	Last Survey/ROOM(S)	InstructionsComments
Compress	sed Gases					
69 (SI69)	Are gas cylinders capable of tipping secured?					Provide Urgent Item notice.
70 (SI70)	Are valve protection caps kept on cylinders when stored?					Note specific issues in comments Provide Urgent Item notice.
71 (SI71)	Are toxic gases stored in a ventilated cabinet/fume hood?					Provide Urgent Item notice.
72 (SI72)	Are oxygen cylinders stored separately from flammable gases and liquids (5' fire wall or 20' distance)?					Note specific issues in comments Provide Urgent Item notice.
		Y	Ν	NA	Last Survey/ROOM(S)	InstructionsComments
Hazardou	s Materials Shipping					
73 (SI73)	Staff that package hazardous materials for shipping is current on training to correctly package, label, and document hazardous materials shipments leaving UC Irvine?					
		Y	Ν	NA	Last Survey/ROOM(S)	InstructionsComments
Other						
74 (SIOther)	Other: (Surveyor, please describe below)					
TOTALS	for Quarterly LBSS Metric					
Additional	Comments:					

Additional Comments:

ENVIRONMENTAL HEALTH & SAFETY LAB INSPECTION PROGRAM LABORATORY SAFETY SURVEY COURTESY NOTIFICATION

Items Requiring Immediate Action - Within 2 Business Days

Principal Investigator: _____

Department:

Items needing attention:

- Clean up spilled chemical residuals(SI#9):
- Clear items currently blocking exits and exit pathways(SI#17):
- Clear items blocking emergency equipment(SI#22):
- Repair broken/frayed electrical cords (submit FMR)(SI#24):
- Repair broken electrical outlet (submit Facilities Management Request)(SI#25):
- Remove items blocking electrical panel (within 3 feet)(SI#30):
- Request EH&S pick-up of failing chemical container SI#46):
- Relocate flammables away from heat/ignition source (~ 3 feet)(SI#52):
- Secure gas cylinder (submit FMR if restraints needed)SI#70):
- Store toxic gas in ventilated cabinet/fume hood(SI#72):
- Other:

Date

Time

Appendix L: Segregation of Incompatible Chemicals

Table M.1 contains a list of incompatible chemicals. The following chemicals, listed in the left column, should not be used with chemicals listed in the right column, except under specially controlled conditions. Chemicals in the left column should not be stored in the immediate area with chemicals in the right column. Incompatible chemicals should always be handled, stored or packed so that they cannot accidentally come into contact with one another. This list is representative of chemical incompatibilities and is not complete, nor are all incompatibilities shown.

Table M.1 – Incompatible Chemicals			
Chemical	Keep Out of C		

Chemical	Keep Out of Contact with:					
	Carbon tetrachloride or other chlorinated hydrocarbons, carbon dioxide and water					
potassium, etc.						
Acetic Acid	Chromic acid, nitric acid, hydroxyl compounds, ethylene glycol, perchloric					
	acid, peroxides and permanganates					
Acetylene	Chlorine, bromine, copper, fluorine, silver and mercury					
Ammonia	Mercury, chlorine, calcium hypochlorite, iodine, bromine and hydrofluoric acid					
Ammonium nitrate	Acids, metal powders, flammable liquids, chlorates, nitrites, sulfur, finely divided organic or combustible materials					
Carbon, activated	Calcium hypochlorite					
Copper	Acetylene and hydrogen peroxide					
Chromic acid	Acetic acid, naphthalene, camphor, glycerin, turpentine, alcohol and flammable liquids					
Chlorine	Ammonia, acetylene, butadiene, butane, methane, propane, hydrogen, sodium carbide, turpentine, benzene and finely divided metals					
Cyanides	Acids - organic or inorganic					
Hydrogen peroxide	Copper, chromium, iron, most metals, alcohols, acetone, organic materials, aniline, nitromethane, flammable liquids and combustible materials					
Hydrogen sulfide	Fuming nitric acid and oxidizing gases					
	Fluorine, chlorine, bromine, chromic acid and sodium peroxide					
benzene, gasoline, turpentine etc.)						
lodine	Acetylene, ammonia and hydrogen					
Nitric acid	Acetic acid, aniline, chromic acid, hydrocyanic acid, hydrogen sulfide, flammable liquids, flammable gases, copper, brass and any heavy metals					
Perchloric acid	Acetic anhydride, bismuth and its alloys, alcohol, paper, wood, ether, oils and grease					
Phosphorous	Oxidizing agents, oxygen, strong bases					
Potassium chlorate	Sulfuric and other acids					
Potassium permanganate Glycerin, ethylene glycol, benzaldehyde and sulfuric acid						
Sodium	Carbon tetrachloride, carbon dioxide and water					
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 and furfural					
Sulfides, inorganic	Acids Sulfuric acid Potassium chlorate, potassium perchlorate and potassium permanganate					

Special Segregation of Incompatible Chemicals

In addition to the segregation noted in Table M.1, dangerously incompatible substances, even in small quantities, should not be stored next to each other on shelves or in such a position that accidental rupture of containers may allow mixing. Table M.2 contains examples of dangerously incompatible substances. Table M.3 contains examples of incompatible oxidizing agents and reducing agents.

Chemical	Keep out of contact with:
Chlorine	Acetylene
Chromic acid	Ethyl alcohol
Oxygen (compressed, liquefied)	Propane
Sodium	Chloroform and aqueous solutions
Nitrocellulose (wet, dry)	Phosphorous
Potassium permanganate	Sulfuric acid
Perchloric acid	Acetic acid
Sodium chlorate	Sulfur in bulk

Table M.2 – Dangerously Incompatible Substances

Table M.3 – Incompatible Oxidizing Agents and Reducing Agents

Oxidizing Agents	Reducing Agents
Chlorates	Ammonia
Chromates	Carbon
Dichromates	Metals
Chromium trioxide	Metal hydrides
Halogens	Nitrates
Halogenating agents	Organic Compounds
Hydrogen peroxide	Phosphorus
Nitric acid	Silicon
Nitrates	Sulfur
Perchlorates	
Peroxides	
Permanganates	
Persulfates	

APPENDIX M: Spill Clean-up Procedures

Laboratory personnel can clean up small spills if trained and competent to do so. Small spills include chemical spills that are up to 1 liter in size and of limited toxicity, flammability and volatility, and mercury spills from broken thermometers (about 1.5 grams). If respiratory protection is needed for spill clean up, the spill is too large to be handled by laboratory personnel – dial **911 or EH&S, 4-6200**. Commercial chemical and mercury spill kits are available, which include protective equipment such as goggles and gloves, neutralizing and absorbing materials, bags, and scoops. You can also make your own spill kits to include the materials described below.

Chemical Spills:

- Sodium Bicarbonate
- Citric Acid
- Vermiculite or other diking material
- pH paper
- 1 pair neoprene or nitrile gloves
- 1 pair goggles
- 1 scoop
- Spill pillows, sorbent pads
- Disposable shoe covers (plastic bags may work)

Mercury Spills:

•

- Disposable gloves
- Disposable shoe covers (plastic bags will work)
- Index card or rubber squeegee
- Disposable syringe or a vacuum trap flask fitted with tubing or Pasteur pipette
- Inactivating solutions and/or powders

Weak Inorganic Acid or Base Spill Clean Up Procedure

- 1. Wear gloves, goggles, laboratory coat and shoe covers.
- 2. To clean-up a spill of weak inorganic acid or base, neutralize the spilled liquid to pH 5 to 8 using a **Neutralizing Agent** such as:
 - Sodium bicarbonate

• Soda ash

Sodium bisulfate

- Citric acid
- 3. Absorb the neutralized liquid with an **Absorbent** such as:
 - Sorbent padsSponges
- Diatomaceous earthPaper towels
- Dry sand
- Vermiculite

Rinse the absorbent pads or sponges in a sink with water. Scoop or place the other absorbent materials into a clear plastic bag. Double bag and tag the bag with a chemical waste label. Fill out the "Chemical Waste Collection" form to request a pickup via the internet at http://www.ehs.uci.edu/programs/enviro/.

Solvent Spill Clean Up Procedure

- 1. Absorb the spill with a non-reactive material such as:
 - Vermiculite
 - Dry sand
 - Paper towels
 - Sponges
- 2. Package as described above. Do not rinse or dispose of any chemicals down the sink or into any drain.

Broken MercuryThermometer Clean Up Procedure

- 1. Clean up the spill immediately after it has occurred.
- 2. Prevent the spread of the spilled mercury. Do not allow people to walk through spill area.
- 3. Wear disposable gloves and shoe covers or place plastic bags over your shoes during the cleanup.
- 4. Push the mercury droplets together into a bead using an index card or rubber squeegee.
- 5. Aspirate the beaded mercury into a disposable syringe, or use a disposable Pasteur Pipette attached with tubing to a vacuum flask to aspirate the mercury into the flask. The flask should contain water. Always have a second vacuum flask between the mercury flask and the house vacuum.
- 6. Chemically inactivate any residual mercury. There are several methods to inactivate the residual mercury including:
 - Use a commercial inactivating powder following its directions for use
 - Sprinkle zinc powder over the spill area. Then moisten the zinc with a 5 to 10 percent sulfuric acid solution until a paste is formed. Scour the contaminated surface and allow the paste to dry. Sweep up the dried paste
 - Wash the contaminated area with a detergent solution. Rinse and then swab the area with a calcium polysulfide solution containing two to four tablespoons of calcium polysulfide per gallon of water

Place the collected mercury and materials used in the clean-up into a clear plastic bag. Double bag and label the waste. Fill out the "Chemical Waste Collection" form to request a pickup via the internet at http://www.ehs.uci.edu/programs/enviro/.

If a large spill occurs, call 911 from a campus phone or from an off-campus or cell phone or EH&S, 4-6200.

Appendix N: Injuries & Medical Treatment Poster

UC IRVINE INJURIES & MEDICAL TREATMENT

CALL 911 if the condition is LIFE THREATENING or REQUIRES IMMEDIATE MEDICAL ATTENTION.

Notify your supervisor or faculty staff if condition is <u>not</u> life threatening. Seek medical attention as follows:

Students (non-UCI employees)

Campus:Student Health Center (East Peltason & Pereira) Call 949-824-5304. Hours: Mon-Fri7:30-5:30

After hours:Go to the nearest urgent care center or hospital emergency room.Be sure to contact Student Health Center for follow-up care as soon as possible.

The Student Health Center (map) is the primary care facility for students covered by the Undergraduate Student Health Insurance Plan (USHIP) and Graduate Student Health Insurance Plan (GSHIP). **Students** with private health insurance instead of USHIP or GSHIP will be charged for services rendered at the Student Health Center and provided a receipt to obtain reimbursement.

For further information, see the Student Health Services website <u>http://www.shs.uci.edu/</u> or see the GSHIP web site <u>http://www.gship.uci.edu/</u>.

Or contact the Insurance Office at (949) 824-2388, (949) 824-9415, (949) 824-4042, (949) 824- 7093

Employees, all student-employees, and volunteers with work-related injuries

Employees or their supervisor must contact UCI Worker's Compensation Desk at 949-824-9152 during regular working hours to obtain medical authorization within 24 hours of <u>any</u> injury.

ALL WORK RELATED INJURIES MUST BE REPORTED via the On-line Incident Form available at the Human Resources website at <u>www.hr.uci.edu</u>, and link to Workers Compensation or call (949) 824-9152

Newport Urgent Care (949) 752-6300

Located off campus (<u>map</u>) - 1000 Bristol Street North, Suite 1-B, Newport Beach (Bristol & Jamboree) Mon-Fri 8am-9pm; Sat & Sun 9am-6pm; Call for after-hours physician.

Occupational Health Clinic at UCI Medical Center (714) 456-8300 Located on campus (map) – Pavilion III, Building 29 Mon-Fri 7:30 am- 5pm, Closed Sat & Sun; After hours - Go to UCIMC emergency room

Occupational Services at Long Beach Memorial Hospital (562) 933-0085 2801 Atlantic Ave., (Memorial West Rehab Entrance) (<u>map</u>) Mon.-Fri. 7am- 5pm; Sat. 9am-5pm; Call for after-hours physician services.

ProCare Work Injury Center (949) 752-1111 17232 Red Hill Ave., Irvine (located off campus, map)

Obtain this poster on the EH&S website at http://www.ehs.uci.edu/MedEmergPoster.pdf.

Appendix O: Laboratory Personal Protective Equipment Assessment Tool

LABORATORY PERSONAL PROTECTIVE EQUIPMENT (PPE) ASSESSMENT TOOL

Principal Investigator's Name:	Work Unit:	
Building(s):	Rooms:	
Lab Contact Name:	Phone:	
Signature of Responsible Person:	Date:	
Completed by:	Signature:	Date

This form must be completed by the PI, Lab Supervisor, or their designee to conduct a laboratory hazard assessment specific to activities in their laboratories. The laboratory hazard assessment identifies hazards to employees and specifies personal protective equipment (PPE) to protect employees during work activities. The PPE assessment tool is online at the EH&S website at http://www.ehs.uci.edu/PPE.html

This assessment consists of two sections.

Section 1: Laboratory PPE Assessment Section 2: Conduct PPE Training

PIs/Lab supervisors are responsible for enforcing PPE requirements. EH&S personnel are available to assist you with completing this form or with reviewing it after you have completed it. EH&S may also be consulted by calling EH&S at 949-824-6200.

Section 1: Laboratory PPE Hazard Assessment

In this section, the PI or Lab Supervisor will:

- Conduct a hazard assessment of the laboratory using the PPE Assessment Tool. The Tool will assist to identify activities when PPE is needed to protect lab staff from exposure to hazards.
- Certify the hazard assessment for the laboratory by signing the table above.
- The following checklist provides an overview of lab activities with associated potential hazards and generic recommendations for PPE. Describe the specific PPE your lab uses for each hazardous activity performed in your lab.

Minimu	CHEMICAL HAZARDS Minimum PPE: Lab coat, long pants or equivalent, safety glasses, closed-toed shoes, disposable 4-mil nitrile gloves or appropriate chemical resistant gloves ⁴ . Operations may need to be performed inside a fume hood		
(√) If applie s	Activity (Modify to fit your needs)	Potential Hazard	Check PPE Selected
	Working with highly diluted (<1%) organic solvents, corrosives or flammable organic compounds.	Irritant.	Safety glasses or goggles where splashing may occur.
	Working with any amount of undiluted corrosives (acids, bases).	Skin or eye damage	 Safety goggles w/ face shield where splashing may occur. Chemical resistant gloves.
	Working with smaller volumes (<1L) of organic solvents or flammable organic compounds.	Potential respiratory, skin, or eye damage; potential poisoning through skin contact.	Use safety glasses or goggles. Use face shield where splashing may occur. Chemical resistant gloves.
	Working with larger volumes (≥1L) of organic solvents or flammable compounds, work which creates a splash hazard. ¹	Potential respiratory, skin, or eye damage; potential poisoning through skin contact. Fire.	 Safety goggles w/ face shield. Use 15-mil thick non-disposable chemical-resistant gloves⁴ (nitrile). Flame-resistant lab coat, if flammable.Refer to SOP.
	Working with small quantity of toxic or hazardous chemicals (solid, liquid, or gas). ^{1, 2}	Potential respiratory, skin, or eye damage; potential poisoning through skin contact.	 Safety glasses/ goggles Light chemical-resistant gloves⁴ Glove with Silver Shield underneath disposable glove. Refer to SOP
	Working with an apparatus with contents under pressure or vacuum (mm of Hg, psi, or torr).	Eye or skin damage.	 Goggles w/face shield. Use blast shield for high risk activities. Chemical-resistant gloves⁴ / apron if chemicals are involved. Refer to SOP
	Working with air or water reactive chemicals.	May give off toxic gases, heat, and energy. Potential inhalation, skin and eye damage. Fire.	 Work in inert atmosphere or inside glove box, where possible. Goggles w/ face shield. Chemical-resistant gloves⁴. Flame retardant lab coat. Blast shield. Refer to SOP.
	Working with pyrophoric materials.	Fire. Potential inhalation, skin and eye damage. Severe burns.	 Work in inert atmosphere or inside glove box. Goggles w/ face shield. Flame retardant lab coat and gloves with inner chemical-resistant gloves. Wear non-synthetic clothing. Refer to SOP.
	Working with potentially explosive chemicals.	Detonation, flying debris, skin and eye damage. Fire.	 Safety goggles w/ face shield and blast shield. Chemical resistant gloves. Flame retardant lab coat. Refer to SOP.

	CHEMICAL HAZARDS Minimum PPE: Lab coat, long pants or equivalent, safety glasses, closed-toed shoes, disposable 4-mil nitrile gloves or appropriate chemical resistant gloves ⁴ . Operations may need to be performed inside a fume hood.			
(√) If applie s	Activity (Modify to fit your needs)	Potential Hazard	Check PPE Selected	
	Working with high temperature equipment or objects.	Burns, fire.	 Safety glasses. Thermal insulated gloves. 	
	Working with cryogenic material.	Burns, frostbite, eye damage.	 Safety glasses w/ face shield. Thermal insulated gloves. 	
	Minor chemical spill cleanup.	Potential skin, eye , respiratory damage.	 Safety glasses or goggles. Chemical-resistant gloves⁴. Chemical-resistant apron. Refer to SOP for additional PPE requirements. Contact EH&S for assistance. 	
	Large chemical spill	Skin or eye damage, respiratory damage	Call 911 for assistance. Report all injuries and fires. Call EH&S for assistance.	

Minimu gloves	RADIOLOGICAL HAZARDS Minimum PPE: Lab coat, long pants or equivalent, safety glasses, closed-toed shoes, disposable 4-mil nitrile gloves or appropriate chemical resistant gloves ⁴ . Operations may need to be performed inside a fume hood.			
(√) If applie s	Activity	Potential Hazard	Applicable PPE ⁴	
	Working with solid radioactive material or solid radioactive waste.	Cell damage, potential spread of radioactive contamination.	 Safety glasses Impermeable⁴ gloves Lab coat Enclosed shoes Long pants. No shorts. Note: This PPE not needed when using sealed radiation sources. 	
	Working with liquid radioactive material (in corrosives, flammables, aqueous liquids – including liquid radioactive waste) or radioactive powders.	Cell damage or spread of contamination, plus hazards for the specific chemical.	 Safety glasses (or goggles for splash hazard) Impermeable gloves Lab coat Enclosed shoes Long pants. No shorts. Note: Select glove type for the applicable chemical hazards. 	
	Working with ultraviolet radiation.	Conjunctivitis, corneal damage, skin burns.	 UV face shield and/or goggles Lab coat. Nitrile gloves if hand exposure is possible. 	

	Working with infrared-emitting equipment (e.g., glass blowing).	Cataracts, burns to cornea.	 Appropriate polycarbonate infrared filter glasses Lab coat.
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Minimu glove	NANOMATERIALS Minimum PPE: Lab coat, long pants or equivalent, safety glasses, closed-toed shoes, disposable 4-mil nitrile gloves or appropriate impermeable glove ⁴ . Work inside a fume hood or HEPA filtered vented enclosure.			
(√) If applie s	Activity (Modify to fit your needs)	Potential Hazard	Additional Recommended PPE ⁴	
	Working with engineered nanomaterials.	Inhalation, chemical exposure, dermal exposure.	 Use P100 dust respirators if working outside a vented enclosure. Nitrile gloves. Review Guidelines for Handling Nanomaterials: https://www.ehs.uci.edu/programs/sop_library/Chemical%20SOPs/UCI%20Nano%20Safe%20Handling.pdf 	

Minimum	LASER HAZARDS Minimum PPE : Lab coat, long pants or equivalent, safety glasses, closed-toed shoes, disposable 4-mil nitrile			
	gloves or appropriate chemical resistant gloves ⁴ .			
(√) If applies	Activity	Potential Hazard	Applicable PPE ⁴	
		OPEN BEAM		
	Performing beam alignment, laser experiment, trouble shooting or maintenance that requires working with an open laser beam, and/or defeating the interlock(s) on any Class 3b or Class 4 laser system.	Eye damage.	Appropriate laser safety goggles/glasses with optical density based on individual beam parameters. EH&S to determine the needed optical density.	
	Viewing a Class 3R laser beam with magnifying optics (including eyeglasses).	Eye damage.	Appropriate laser safety goggles/glasses with optical density based on individual beam parameters. EH&S to determine the needed optical density.	
	Working with a Class 3b open beam laser system with the potential for producing direct or specular (mirror-like) reflections.	Eye damage.	Appropriately shaded goggles/glasses with optical density based on individual beam parameters. EH&S to determine the needed optical density.	
	Working with a Class 4 open beam laser system with the potential for producing direct, specular, <u>or</u> diffuse reflections.	Eye damage, skin damage.	 Appropriate laser safety goggles/glasses with optical density based on individual beam parameters. <i>EH&S to determine the needed optical</i> <i>density.</i> Long sleeved shirt (tightly wound fabric) Lab coat Nitrile gloves 	
	NON-BEAM			
	Handling dye laser materials, such as powdered dyes, chemicals, and solvents.	Cancer, explosion, fire.	 ☐ Impermeable gloves⁴, ☐ Safety glasses ☐ Flame-resistant lab coat or coveralls. 	

Maintaining and repairing power sources for Class 3B and Class 4 laser systems.	Electrocution, explosion, fire.	 Electrical isolation mat Flame-resistant lab coat Insulated gloves Safety glasses Coveralls Implement Lockout/Tagout procedures. Refer to SOP. Contact EH&S for assistance.
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Minimum	PHYSICAL HAZARDS Minimum PPE: Lab coat, long pants or equivalent, safety glasses, closed-toed shoes, disposable 4-mil nitrile gloves.		
(√) If applies	Activity (Modify to fit your needs)	Potential Hazard	Additional Recommended PPE ⁴
	Working with cryogenic liquids.	Major skin, tissue, or eye damage.	Goggles and face shield Cryogenic or loose fitting heavy leather gloves Cryogenic apron
	Removing freezer cryovials from liquid nitrogen	Vials may explode upon rapid warming. Cuts to face/neck and frostbite to hands.	 Safety glasses or goggles and face shield Cryogenic or loose fitting heavy leather gloves
	Working with very cold equipment or dry ice.	Frostbite, hypothermia.	Safety glasses Cryogenic or heavy leather gloves (possibly warm clothing)
	Working with hot liquids, heating equipment, open flames (autoclave, Bunsen burner, water bath, oil bath).	Burns resulting in skin or eye damage.	Safety glasses Goggles for hot liquids Autoclave gloves (impermeable insulated gloves for liquids, steam)
	Glassware washing.	Lacerations.	Safety glasses
	Working with loud equipment, noises, sounds, alarms, etc.	Potential ear damage and hearing loss.	Earplugs or ear muffs as necessary. Contact EH&S for noise exposure assessment.
	Working with a centrifuge.	Imbalanced rotor can lead to broken vials, cuts, potential exposure to aerosols.	 Centrifuge rotor should be opened inside fume hood or biosafety cabinet if potential for broken vials exists. Goggles Appropriate gloves.
	Working with a sonicator.	Ear damage, exposure to aerosols.	 Place inside fume hood or biosafety cabinet to capture aerosols. Goggles Impermeable gloves⁴.
	Working with sharps.	Cuts, exposure to aerosols.	 Use tongs for broken glass and designated sharps container for contaminated wastes Cut resistant gloves (Kevlar) with nitrile underneath.
	Working with compressed gases inside environmental chambers	Asphyxiation or toxic gas exposure	NOT ALLOWED. Contact EH&S for guidance. Review SOP and install oxygen sensors inside chamber.

	BIOLOGICAL HAZARDS ⁶ Minimum PPE: Lab coat, closed-toed shoes, disposable 4-mil nitrile gloves.		
(√) If applies	Activity (Modify to fit your needs)	Potential Hazard	Additional Recommended PPE ⁴
	Working with human blood, body fluids, cell lines (primary or established), tissues, or blood borne pathogens (BBP). ⁶	Exposure to infectious material.	 Perform inside a Biosafety cabinet (BSC) Latex or nitrile gloves Lab coat or gown
	Working with preserved animal and/or human specimens.	Exposure to infectious material or preservatives.	 Perform in a BSC Safety glasses required if performed outside of a BSC Impermeable glove⁴ for preserved specimens according to preservative used Lab coat Disposable gown
	Working with radioactive human blood, body fluids, or blood borne pathogens (BBP).	Cell damage, potential spread of radioactive contaminants, or potential BBP exposure to infectious material.	 Perform in a BSC Latex or nitrile gloves Lab coat Gown
	Working with agents or recombinant DNA classified as Risk Group 1 and requiring Biosafety Level 1 containment	Biological agents that typically pose a minimal potential for infection via injection, skin exposure, ingestion or inhalation.	 Safety glasses or goggles for protection from splash or other eye hazard Latex or nitrile gloves Lab coat Disposable gown
	Manipulation of recombinant DNA, cell lines, viruses, bacteria, or other organisms classified as Risk Group 2 and requiring Biosafety Level 2 (BSL-2). ⁶	Biological agents that pose a moderate potential for infection via injection, skin exposure, ingestion or inhalation.	 Perform in a BSC Latex or nitrile gloves Lab coat Surgical gown
	Manipulation of infectious materials classified as Risk Group3 but manipulated in a BSL 2 facility with BSL-3 practices (BSL 2+)	Biological agents that pose a moderate/serious potential for infection via injection, skin exposure, ingestion or inhalation.	 Safety glasses or goggles for protection from splash or other eye hazard nitrile gloves (double) Lab coat Disposable gown (preferred) that ties in the back Respirator if indicated
	Manipulation of infectious materials classified as Risk Group 3 and requiring Biosafety Level 3 (BLS-3) containment.	Biological agents that pose a serious or lethal potential for infection via injection, skin exposure, ingestion or inhalation	 Safety glasses or goggles for protection from splash or other eye hazard Nitrile gloves (double) Full disposable coverall suit (preferred) Respirator Shoe cover or dedicated shoe.
	Working with live animals (Animal Biosafety Level 1, ABL- 1).	Animal bites, allergies.	 Safety glasses or goggles for protection from splash or other eye hazard Nitrile or vinyl gloves for broken skin Lab coat or gown Consider need for wire mesh or Kevlar glove

	BIOLOGICAL HAZARDS ⁶ Minimum PPE: Lab coat, closed-toed shoes, disposable 4-mil nitrile gloves.			
(√) If applies	Activity (Modify to fit your needs)	Potential Hazard	Additional Recommended PPE ⁴	
	Working with live animals (Animal Biosafety Level 2, ABL- 2). ⁶	Animal bites, exposure to infectious material, allergies.	 Safety glasses or goggles for protection from splash or other eye hazard Nitrile or vinyl gloves Disposable gown Shoe covers Consider need for wire mesh or Kevlar glove 	
	Working with live animals (Animal Biosafety Level 2+, ABL-2+). ⁶	Animal bites, exposure to infectious material, allergies.	 Safety glasses or goggles for protection from splash or other eye hazard Nitrile or vinyl gloves Disposable gown Shoe covers N-95 respirator as indicated Consider need for wire mesh or Kevlar glove. 	
	Working with live animals (Animal Biosafety Level 3, ABL- 3). ⁶	Animal bites, exposure to infectious material, allergies.	 Safety glasses or goggles for protection from splash or other eye hazard Nitrile or vinyl gloves Disposable gown Shoe covers Respirator (N-95 or PAPR) Consider need for wire mesh glove 	

Additional Guidance

1. When materials have a potential for becoming airborne, use a chemical fume hood or other engineering control whenever possible. Activities, with a potential to generate airborne contaminants, not conducted inside a chemical fume hood or with another engineering control (such as a local exhaust at the workbench) should be evaluated to determine if the activity presents a respiratory hazard. In this case a respirator may be required and a respiratory protection program must be in place per EH&S. Guidance can be found at <u>www.ehs.uci.edu</u>.

2. In addition to engineering controls and PPE, consider personal clothing that provides adequate skin coverage.

3. Manipulations of dust-producing solids should be evaluated for the need to use respiratory protection.

4. Chemical-resistant gloves are to be selected based on the specific chemical(s) used and manufacturer's glove permeation and compatibility charts. http://www.coleparmer.ca/techinfo/techinfo.asp?htmlfile=ChartDisposGloves.htm&ID=56 5. All PPE must be inspected prior to use, during, after use. Re-usable equipment must be decontaminated or disposed if not feasible.

6. Use a biosafety cabinet to minimize exposure. Activities that cannot be conducted inside biosafety cabinet should be separately evaluated by the EH&S Biosafety Office. For BSL-3 or ABL-3 activities, the PPE requirements will be addressed by the BSL-3 facility.

Section 2: Conduct PPE Training

PPE training consists of **lab specific training** conducted by the lab supervisor. Documentation is required to indicate training has been conducted.

Step 1

The PI or lab supervisor assures that the employees have completed the UCLC Safety Training Self-Assessment and all applicable safety training courses.

Step 2

- a. The PI, lab supervisor, or their designee reviews the **completed** *Lab PPE Assessment Tool* (this document) with the employee. It describes the tasks in the lab when employees need PPE to protect themselves from exposure to hazards. In this step, the hazard assessment is used as a training tool.
- b. While discussing lab activities and the associated hazards with lab staff, the supervisor will address how their lab obtains PPE, what types of PPE are used in the lab and for which tasks, where and how the PPE is stored and maintained, how to properly use the PPE, and discuss any limitations of the PPE. The supervisor should also discuss general PPE safety practices, including not wearing PPE outside of lab hazard areas (e.g. hallways and eating areas).
- c. Each research staff will sign below acknowledging that they have reviewed the PPE assessment tool.

Step 3

Conduct and document refresher training whenever the hazard assessment is updated.

PPE Hazard Assessment Tool Training Acknowledgement:

I have read, asked questions, and understand the PPE requirements for the activity/materials described herein.

PI SIGNATURE/LAB SUPERVISOR	DATE
TRAINEES NAME	DATE

The PPE assessment tool is online at the EH&S website at http://www.ehs.uci.edu/PPE.html

Appendix P: Acutely Toxic Chemicals SOP

Standard Operating Procedure

Acutely Toxic Chemicals

Department:	????
Date SOP written:	????
Date SOP approved by PI/lab supervisor:	????
Principal Investigator:	????
Internal Lab Safety Coordinator/Manager:	????
Lab Phone:	????
Office Phone:	????
Emergency Contact:	????
Location(s) covered by this SOP:	????

Type of SOP:

Process
Hazardous Chemical

X Hazardous Class

Purpose

The purpose of this standard operating procedure is to acquaint you with chemicals that are acutely toxic.

A list of the acutely toxic chemicals used in this lab is shown in the Appendix at the end of this document.

Acute toxicity – From *Prudent Practices in the Laboratory: Handling and Management of Chemical Hazards (section 4.C.2.1, Acute Toxicants)* The National Academies Press: Washington, DC, 2011:

"<u>Acute toxicity is the ability of a chemical to cause a harmful effect after a single exposure</u>. Acutely toxic agents cause local toxic effects, systemic toxic effects, or both, and this class of toxicants includes corrosive chemicals, irritants, and allergens (sensitizers)."

Factors that affect toxicity:

- 1. **Dosage**: Concentration of the substance required to cause harm
- 2. Route of Exposure: how the substance enters your body
 - a. Inhalation
 - b. Dermal (Skin) Absorption
 - c. Ingestion
 - d. Injection
- 3. **Duration of Exposure:** Period of time spent exceeding established Permissive Exposure Limits (PEL).

Resources Relevant to Established Permissive Exposure Limits (PELs)

- National Institute for Occupational Safety and Health (NIOSH) Pocket Guide to Chemical Hazards<u>http://www.cdc.gov/niosh/npg/</u>
- Information regarding the Permissive Exposure Limit (PEL) of most every chemical may be found in the following sections of the Material Safety Data Sheet (MSDS)
 - OSHA Formatted MSDS:
 - Section II Hazard Ingredients/Identity Information
 - Section VI Health Hazard Data
 - ANSI Formatted MSDS:
 - Section 2 Hazards Identification
 - Section 3 Composition, Information on ingredients
 - Section 8 Exposure Controls / Personal Protection

Definition of Chemical Group

Toxins are defined by toxicity parameters derived from animal studies and/or human exposure from accidental poisoning. A chemical is considered highly toxic considered if it fits within any of the following categories:

- 1. A chemical with a median lethal dose (LD₅₀) of 50 mg or less per kg of body weight when administered orally to albino rats weighing between 200 and 300 g each.
- 2. A chemical with a median lethal dose (LD₅₀) of 200 mg or less per kg of body weight when administered by continuous contact for 24 hours (or less if death occurs within 24 hours) with the bare skin of albino rabbits weighing between 2 and 3 kg each.
- 3. A chemical that has a median lethal concentration (LC_{50}) in air of 5000 ppm by volume or less of gas or vapor, or 50 mg per liter or less of mist, fume, or dust, when administered by continuous inhalation for 1 hour (or less if death occurs within 1 hour) to albino rats weighing between 200 and 300 g each.

In some cases these materials may also have carcinogenic properties and/or pose reproductive hazards.

Acute Toxicity Hazard Level:

Hazard Level	Toxicity Rating	Oral LD₅₀ (rats, per kg)	Skin Contact LD₅₀ (rabbits, per kg)	Inhalation LC ₅₀ (rats, ppm for 1 h)	Inhalation LC₅₀ (rats, mg/ m³ for 1 h)
High	Highly toxic	<50 mg	<200 mg	<200	<2,000
Medium	Moderately toxic	50 – 500 mg	200 mg – 1 g	200 to 2,000	2,000 - 20,000
Low	Slightly toxic	500 mg – 5 q	1 – 5 g	2,000 – 20,000	20,000 - 200,000

SOURCE: Prudent Practices in the Laboratory: Handling and Management of Chemical Hazards (section 4.C.2.1, Acute Toxicants)

Probable Lethal Dose for Humans:

Toxicity Rating	Animal LD ₅₀ (per kg)	Lethal Dose When Ingested by 70-kg (150-lb) Human	
Extremely toxic	<5 mg	A taste (<7 drops)	
Highly toxic	5 – 50 mg	Between 7 drops and 1 tsp	
Moderately toxic	50 – 500 mg	Between 1 tsp and 1 oz	
Slightly toxic	500 mg – 5 g	Between 1 oz and 1 pint	
Practically nontoxic	>5 g	>1 pint	

SOURCE: Prudent Practices in the Laboratory: Handling and Management of Chemical Hazards (section 4.C.2.1, Acute Toxicants)

- **LD**₅₀: The amount of a chemical that when ingested, injected, or applied to the skin of test animals under controlled laboratory conditions will kill one-half (50%) of the animals.
- **LC**₅₀ : The concentration of the chemical in air that will kill 50% of the test animals exposed to it. (usually used for volatile compounds)

Common classes of acute toxins (from *Prudent Practices in the Laboratory: Handling and Management of Chemical Hazards*)

<u>1. *Corrosives.*</u> These compounds can destroy living tissues (skin, eyes, digestive/respiratory tracts, etc.) upon contact, and are among the most common toxins encountered in laboratories. Some examples:

strong acids/bases (e.g., sulfuric acid, HF, sodium hydroxide solutions) strong dehydrating agents (e.g., P₂O₅) strong oxidizing agents (e.g., hydrogen peroxide) certain gases (e.g., chlorine, bromine, ammonia, chloramines, nitrogen dioxide) certain solids (e.g., phosphorus, phenol)

<u>2. Irritants.</u> These non-corrosive chemicals cause burns, swelling, or tissue redness at sites of contact; the effects are reversible in most cases. Common laboratory irritants include formaldehyde, iodine, and benzoyl chloride.

<u>3. Allergens (sensitizers).</u> These compounds cause adverse immune reactions, often from prior exposure. While most allergic reactions are delayed (and usually localized to the skin, where it becomes red/swollen/itchy), some exposures may result in anaphylactic shock—a severe, immediate reaction that can result in death. Individuals vary widely in their tendency to become sensitized to allergens, but some documented cases include diazomethane, DCC, phenol derivatives, various isocyanates, formaldehyde, benzylic/allylic halides, metals, and acid anhydrides.

<u>4. Asphyxiants</u>. These substances interfere with the transport of oxygen to vital organs. Examples include large doses of acetylene, carbon dioxide, argon, helium, ethane, nitrogen, and methane. These gases displace oxygen from the air being breathed. Some asphyxiants can also combine with hemoglobin, reducing the capacity of blood to transport oxygen. Examples of these include HCN, CO, and certain cyanides.

<u>5. Neurotoxins</u>. These chemicals adversely impact the function of the nervous system, and can result in either permanent or reversible damage. Some symptoms of neurotoxicity include slurred speech and staggered walking. Examples of neurotoxins include mercury and its derivatives, organotin compounds, organophosphate pesticides, carbon disulfide, xylene, trichloroethylene, and n-hexane.

<u>6. Reproductive/developmental toxins</u>. These compounds cause chromosomal damage (mutagens) or teratogenic (malformation) effects on fetuses or other aspects of reproduction, including fertility. These compounds are also covered under a separate SOP. Examples of such toxins include halogenated hydrocarbons, nitroaromatics, mercury, bromine, and some ethylene glycol ethers.

<u>7. Carcinogens.</u> These compounds are known cancer-causing substances and are covered under a separate SOP.

<u>Other compounds with high levels of acute toxicity</u> (from *Prudent Practices*): acrolein, arsine, diborane gas, dimethylmercury, methyl fluorosulfonate, nickel carbonyl reagents, nitrogen dioxide, osmium tetroxide, ozone, phosgene, sodium azide, sodium cyanide (and other cyanide salts).

<u>This list is by no means exhaustive</u>. Before beginning experimentation one should consult the relevant material data safety sheets to ascertain the individual toxicities of the reagents at play.

Other Resources Relevant to the Toxicity of Common Laboratory Chemicals

• National Library of Medicine: Specialized Information Services: <u>http://sis.nlm.nih.gov/chemical.html</u>

Potential Hazards/Toxicity – Burns, Poisoning, Asphyxiation, Death

Exposure to toxic compounds can result in severe burns or tissue damage, reproductive problems, and/or neurological damage. Poisoning and/or asphyxiation due to the displacement of breathable air can also result in death.

Personal Protective Equipment (PPE)

At a minimum the following PPE must be worn at all times:

1. Eye Protection

- a. Safety glasses or splash goggles that meet the ANSI Z.87.1 1989 standard
 - i. When there is the potential for splashes, goggles must be worn, and when appropriate, a face shield. Face shields protect the face and are work WITH appropriate eye protection. Face shields are not a substitute for glasses or goggles.
- b. Ordinary prescription glasses will NOT provide adequate protection unless they also meet this standard.

2. Skin and Body Protection (including Hand Protection)

Skin, face, and eyes must be protected with appropriate gloves and eyewear

a. Lab coat

For hazardous chemicals that are toxic via skin contact/ absorption, additional protective clothing (i.e. over sleeves) is appropriate where chemical contact w/ body/ skin is foreseeable.

- i. Fully extend sleeves to the wrists.
- ii. Buttoned at all times.
- iii. If significant risk of fire exists, a Nomex® lab coat with a higher flammability resistance rating should be worn.
- b. Gloves
 - i. When handling hazardous chemicals or contacting potentially contaminated surfaces, protective gloves are to be worn. For proper selection of glove material, review chemical Safety Data Sheet and glove manufacturers' selection guidance charts.
 - ii. Consider using Teflon laminated Silver Shield gloves with disposable nitrile gloves for highly aggressive chemicals. See glove chart at <u>www.northsafety.com</u>.
 - iii. Never re-use disposable gloves.
- c. Close toed shoes
- d. Covered legs

3. Respirator Protection

Respiratory protection is generally not required for lab research, provided the appropriate engineering controls are employed. Respirators should be used only under any of the following circumstances:

- As a last line of defense (i.e., after engineering and administrative controls have been exhausted).
- When Permissible Exposure Limit (PEL) has exceeded or when there is a possibility that PEL will be exceeded.
- Regulations require the use of a respirator.

- An employer requires the use of a respirator.
- There is potential for harmful exposure due to an atmospheric contaminant (in the absence of PEL)
- As PPE in the event of a chemical spill clean-up process

Lab personnel intending to use/wear a respirator mask must be trained and fit-tested by EH&S. This is a regulatory requirement. If you think that your process may require respirator use, contact EH&S for assistance (<u>http://www.ehs.uci.edu/programs/ih/respiratory.html</u>)

Additional PPE may be required if procedures or processes present additional risk.

Hygiene Measures

Wash thoroughly and immediately after handling. Remove contaminated clothing and wash before reuse.

Engineering Controls

The following is a general plan for Highly Acute Toxic Materials:

1. Use a properly functioning, certified chemical fume hood when handling the material. If the process does not permit the handing of such materials in a fume hood, contact EH&S for reviewing the adequacy of ventilation measures.

2. Use containment devices (such as glove boxes) when: (i) volatilizing these substances, (ii) manipulating substances that may generate aerosols, and (iii) performing laboratory procedures that may result in uncontrolled release of the substance.

3. Use high efficiency particulate air (HEPA) filters, carbon filters, or scrubber systems with containment devices to protect effluent and vacuum lines, pumps, and the environment whenever feasible.

4. Use ventilated containment to weigh out solid chemicals. Alternatively, the tare method can prevent inhalation of the chemical. While working in a laboratory hood, the chemical is added to a pre-weighed container. The container is then sealed and can be re-weighed outside of the hood. If chemical needs to be added or removed, this manipulation is carried out in the hood. In this manner, all open chemical handling is conducted in the laboratory hood.

5. Transport materials between locations using a non-breakable bottle carrier whenever possible.

Vacuum Protection

Evacuated glassware can implode and eject flying glass, and splattered chemicals. Vacuum work involving acutely toxic chemicals must be conducted in a fume hood, glove box or isolated in an acceptable manner. Mechanical vacuum pumps must be protected using cold traps and, where appropriate, filtered to prevent particulate release. The exhaust for the pumps must be vented into an exhaust hood.

Administrative Controls

1. Never work alone. At least one other person must be **Safety shielding**. Safety shielding is required any time there is a risk of explosion, splash hazard or a highly exothermic reaction. All

manipulations of acutely toxic chemicals that pose this risk should occur in a fume hood with the sash in the lowest feasible position. Portable shields which provide protection to all laboratory occupants are acceptable.

2. Eliminate or substitute a less hazardous material when possible.

3. Design your experiment to use the least amount of material possible to achieve the desired result.

4. Verify your experimental set-up and procedure prior to use.

5. Inform colleagues that this material will be used and where. Label the work area with a sign saying "XXXX Use Area."

6. Only use if the area is equipped with a certified eye wash/safety shower within ten seconds of travel.

7. Ensure that all use details are recorded in a logbook containing the date, user, amount used, and current quantity on hand.

Required Training / Approvals

All work with Highly Acute Toxic Materials requires the following prior to beginning work:

1. Approval from the Principal Investigator and documentation of appropriate training.

2. Familiarity with the lab's Chemical Hygiene Plan and specific SOP's in the lab SOS binder.

3. Appropriate Laboratory Safety training and documentation. (Note that additional laboratory specific training may be needed to support this SOP (e.g., working with HF). In these cases, the PI must be consulted and the signed and dated training documents must be uploaded into the lab's SOS binder. Examples include Safety Data Sheets, experimental procedures, journal articles, etc.)

4. Adherence to this SOP.

5. Examination of relevant Safety Data Sheets (formerly referenced as Material Safety Data Sheets).

6. Review of the Center for Disease Control's, National Institute for Occupational Safety and Health (NIOSH) web site - http://www.cdc.gov/niosh/ for relevant information on the material being used.

7. Review of Prudent Practices in the Laboratory: Handling and Management of Chemical Hazards (section <u>section 4.C.2.1, "Acute Toxicants"</u> 6D Working with Substances of High Toxicity))

8. Completion of UCI Compressed Gas Safety if the chemical is a compressed gas.

First Aid Procedures

Chemicals may enter the body via four routes: inhalation, ingestion, injection, or contact with skin/eyes.

With each route of exposure, the likelihood of injury depends on the toxicity of the chemical involved, the concentration of the material, and the duration of contact.

Consult the SDS for the reagent being used. General first aid procedures for hazardous chemicals typically include:

If inhaled

Move person into fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Seek medical aid immediately.

In case of skin contact

Wash skin with soap and water for at least 15 minutes while removing contaminated clothing and shoes. Wash clothing before reuse. Thoroughly clean shoes before reuse. Consult a physician.

In case of eye contact

Flush eyes with plenty of water for at least 15 minutes. Consult a physician.

If swallowed

Do NOT induce vomiting unless directed by medical personnel. Never give anything by mouth to an unconscious person. Seek medical attention immediately.

Special Handling and Storage Requirements

When working with highly acute toxins, establish a designated area where limited access, special procedures, knowledge, and work skills are required. A designated area can be the entire laboratory, a specific laboratory workbench, or a laboratory hood. Designated areas must be clearly marked with signs that identify the chemical hazard and include an appropriate warning; for example: WARNING! HIGHLY ACUTE TOXIC MATERIAL WORK AREA!

Store toxic materials in unbreakable secondary containment. If the chemical is volatile (or could react with moisture in air to form volatile toxic compounds), containers should be stored in ventilated areas. All containers of highly toxic substances should be clearly labeled; incompatible materials should not be stored together.

Spill and Accident Procedure

Experiments conducted with highly toxic chemicals should be carried out in work areas designed to contain accidental releases. Trays and other containers should be used to contain spills.

Chemical Spill Dial 911

Spill – Assess the extent of danger. Help contaminated or injured persons if it is safe to do so. Evacuate the spill area. Avoid breathing vapors. If possible, confine the spill to a small area using a spill kit or absorbent material. Keep others from entering contaminated area (e.g., use caution tape, barriers, etc.).

Small – Consider any spill of highly acutely toxic chemicals as a large spill.

Large – Dial 911 and EH&S at x46200 for assistance.

Chemical Spill on Body or Clothes – Remove clothing and rinse body thoroughly in emergency shower for at least 15 minutes. Seek medical attention. *Notify supervisor and EH&S at x46200 immediately.*

Chemical Splash Into Eyes – Immediately rinse eyeball and inner surface of eyelid with water from the emergency eyewash station for 15 minutes by forcibly holding the eye open. Seek medical attention. *Notify supervisor and EH&S at x46200 immediately.*

Article III.

Article IV. Medical Emergency Dial 911

a. Life Threatening Emergency, Business Hours, After Hours, Weekends and Holidays – Dial **911** CALL 911 if the condition is LIFE THREATENING or REQUIRES IMMEDIATE MEDICAL ATTENTION.. *Note: All serious injuries <u>must</u> be reported to EH&S at x46200 within 8 <i>hours.* Complete online incident report at <u>https://www.ehs.uci.edu/apps/hr/index.jsp</u>

b. Non-Life Threatening Emergency – Notify your supervisor or faculty/staff if condition is not life threatening.

c. Needle Stick/puncture Exposure (as applicable to chemical handling procedure) – Wash the affected area with antiseptic soap and warm water for 15 minutes. For mucous membrane <u>exposure</u>, flush the affected area for 15 minutes using an eyewash station.

ALL WORK RELATED INJURIES MUST BE REPORTED via the On-line Incident Form <u>https://www.ehs.uci.edu/apps/hr/index.jsp</u> or call Human Resources, Workers Compensation (949) 824-9152.

Decontamination/Waste Disposal Procedure

Work area: Decontamination procedures vary depending on the material being handled. The toxicity of some materials can be neutralized with other reagents. All surfaces should be wiped with the appropriate cleaning agent following dispensing or handling. Waste materials generated should be treated as hazardous waste. After each use, wipe down the immediate work area and equipment to prevent accumulation of chemical residue and thoroughly decontaminate the designated area before resuming normal laboratory work in the area.

Equipment: Decontaminate vacuum pumps or other equipment (glassware) before removing them from the designated area.

Personnel: Upon leaving the designated area, remove any personal protective equipment worn and wash hands, forearms, face, and neck. Immediately after working with highly acutely toxic materials, remove gloves and wash hands and arms with soap and water.

General hazardous waste disposal guidelines:

Label Waste

 Hazardous waste labels must be placed on the hazardous waste container upon the start of accumulation. Labels are available online at <u>www.ehs.uci.edu/programs/enviro/.</u>

Store Waste

- Hazardous waste containers must be kept closed, except when adding waste.
- Hazardous waste containers must be stored in secondary containment to adequately contain all of the contents of the container.
- Hazardous waste containers must be inspected weekly for signs of leaks, corrosion, or deterioration.

Dispose of Waste

- Hazardous waste must be transferred to EH&S for disposal within 6 months of being generated.
- Empty Containers: At no time should full or partially full containers be placed in the trash. For more information on empty container management visit <u>www.ehs.uci.edu/programs/enviro/</u>.
- Hazardous Waste Disposal:
 - Visit <u>www.ehs.uci.edu/programs/enviro/</u>.
 - Fill out the "Chemical Waste Collection" form.
 - EH&S will pick up your waste within 1-3 days.
- Do not dispose of chemicals by pouring them down the drain or placing them in the trash.
- Do not use fume hoods to evaporate chemicals.

Safety Data Sheet (SDS) Location

Online SDSs can be accessed at http://www.ehs.uci.edu/msds.html.

Designated Area

Experiments involving highly toxic chemicals should be confined to a fume hood.

Lab-Specific Procedures

Lab-specific procedures for this class of chemicals include storing, dispensing, use in chemical reactions, use in processes (e.g., distillation, rotary evaporation, or chromatography), and disposal. Appropriate personal protective equipment and engineering controls are to be used.

General safety practices apply when working with highly toxic materials, but additional precautions are needed to set up multiple lines of defense to minimize the risks posed by these substances. (Adapted from Prudent Practices in the Laboratory: Handling and Management of Chemical Hazards (section 4.C.2.1, "Acute Toxicants" and section, 6.D "Working with Substances of High Toxicity") The National Academies Press: Washington, DC, 2011.)

 PLAN carefully and think ahead. You must have an understanding of the intrinsic hazards of the substances being used or potentially formed in any reaction. NEVER work with a reagent you are unfamiliar with without consulting your PI or an experienced coworker and relevant SDS information, toxicological data, or other safety information. Always consider substituting less toxic substances for highly toxic materials and using only the smallest amount possible. For substances with unusual potential hazards, consult A Comprehensive Guide to the Hazardous Properties of Chemical Substances (Patanik, 2007) or the NIOSH website (see above). Plan for careful management of the substances through their life cycle—from acquisition and storage through safe disposal. Choose equipment and glassware that are easy to clean and decontaminate. You must also know the signs and symptoms of acute exposure, and know how to respond in an emergency.

Note: The combination of the toxic effects of two substances may be *significantly greater* than the toxic effect of either substance alone. Additionally, the possibility of generating toxic reaction *products* must also be considered during the planning phase.

- 2. <u>Never work alone</u>. It is *essential* that more than one person be present when highly toxic materials are handled. Additionally, all individuals working in the vicinity must be familiar with the hazards of the experiments being conducted as well as the appropriate emergency responses.
- 3. <u>Confine procedures involving highly toxic chemicals that can generate dust, vapors, or aerosols to a chemical hood, glovebox, or other containment device</u>. Experiments involving highly toxic chemicals, including transfers to reaction vessels, should be confined to a designated work area (e.g., fume hood). This area should be recognized as a place where special training/precautions/skill are required. When toxic chemicals are used in a chemical hood, the sash should be at a proper level. When working in a glove box, it should be operated under negative pressure. Post signs to alert others of particularly dangerous experiments.
- 4. <u>Wear gloves and safety glasses</u> for protection. Select gloves to make sure they are impervious to the chemical being used and correct thickness. Check gloves for integrity and appropriate composition before use. Safety glasses with side shields are a minimum standard. In some cases, face shields or respirators may be required.
- 5. <u>Isolate equipment</u> for handling of highly toxic chemicals, including vacuum pumps.
- 6. <u>Practice good hygiene</u>. Cleanliness, order and good housekeeping practices create an intrinsically safer workplace. After using toxic materials, wash hands/neck/arms/face with soap and water. Equipment that might be contaminated (including gloves) must not be removed from the area reserved for handling toxic materials without complete decontamination. Wipe down the immediate work area and equipment to prevent accumulation of chemical residue and thoroughly decontaminate the designated area before resuming normal laboratory work in the area.

If you have questions concerning any item listed in this procedure, consult with your Research Advisor or EH&S.

Specific acutely toxic chemical with their own SOP

Some acutely toxic chemicals may have specific SOPs that are located in the Appendix or in the laboratory's Safety on Site binder.

Prior Approval Required

Any deviation from this SOP requires approval from PI.

Documentation of Training (signature of all users is required)

- Prior to conducting any work with acutely toxic chemicals, designated personnel must provide training to his/her laboratory personnel specific to the hazards involved in working with this substance, work area decontamination, and emergency procedures.
- The Principal Investigator must provide his/her laboratory personnel with a copy of this SOP and a copy of the SDS provided by the manufacturer.
- The Principal Investigator must ensure that his/her laboratory personnel have attended appropriate laboratory safety training or refresher training within the last one year.

I have read and understand the content of this SOP:

Name	Signature	Date

APPENDIX:

Acutely Toxic Chemicals Used in Lab

????

Appendix Q: Acutely Toxic Gases SOP

Standard Operating Procedure

Acutely Toxic Gases

Department:	????
Date SOP written:	????
Date SOP approved by PI/lab supervisor:	????
Principal Investigator:	????
Internal Lab Safety Coordinator/Manager:	????
Lab Phone:	????
Office Phone:	????
Emergency Contact:	????
Location(s) covered by this SOP:	????

Type of SOP:
□ Process

Hazardous Chemical

X Hazardous Class

Purpose

The purpose of this standard operating procedure is to acquaint you with gases that are acutely toxic.

A list of the acutely toxic gases used in this lab is shown in the Appendix at the end of this document.

1. HAZARD OVERVIEW

There is a broad spectrum of toxic compressed gases. Increased recognition of the hazards associated with the transportation, operation, and storage of these gases is essential.

2. HAZARDOUS CHEMICAL(S)/CLASS OF HAZARDOUS CHEMICAL(S)

Acutely toxic gases are those that may cause significant acute health effects at low concentrations. Health effects may include severe skin or eye irritation, pulmonary edema, neurotoxicity, or other potentially fatal conditions. The criteria used to establish the list are: (1) A National Fire Protection Association (NFPA) health rating of 3 or 4; (2) An NFPA health rating of 2 with poor physiological warning properties; (3) Pyrophoric (self-igniting) characteristics; or (4) Extremely low occupational exposure limits in the absence of an NFPA health rating.

The acutely toxic gases below are listed in the Settlement Agreement, with CAS numbers in parentheses:

Ammonia (7664-41-7), arsenic pentafluoride (7784-36-3), arsine (7784-42-1), boron trichloride (10294-34-5), boron trifluoride (7637-07-2), carbon monoxide (630-08-0), chlorine (7782-50-5), cyanogen (460-19-5), cyanogen chloride (506-77-4), diazomethane (334-88-3), diborane (19287-45-7), ethylene oxide (75-21-8), fluorine (7782-41-4), germane (7782-65-2), hexaethyl tetraphosphate (757-58-4), hydrogen bromide (10035-10-6), hydrogen chloride (7647-01-0), hydrogen fluoride (7664-39-3), hydrogen selenide (7783-07-5), hydrogen sulfide (7783-06-4), methyl mercaptan (74-93-1), nitric oxide (10102-43-9), nitrogen dioxide (10102-44-0), dinitrogen tetroxide (10544-72-6), oxygen difluoride (7641-19-0), selenium hexafluoride (7783-79-1), silane (7803-65-5), stibine (7803-52-3), sulfur tetrafluoride (7783-60-0), trimethylsilyldiazomethane (18107-18-1).

3. PERSONAL PROTECTIVE EQUIPMENT (PPE)

At a minimum, the following PPE must be worn at all times:

1. Eye Protection

ANSI-compliant safety glasses with side shields, or chemical splash goggles.

When there is the potential for exposure, goggles must be worn.

2. Skin Protection

a. Lab coat. For hazardous chemicals that are toxic by skin contact/absorption, additional protective clothing (i.e., oversleeves) is appropriate where chemical contact with body/skin is foreseeable.

- i. Fully extend sleeves to the wrists.
- ii. Buttoned at all times.
- iii. If significant risk of fire exists, a flame-resistant lab coat should be worn.
- b. Non-synthetic clothing should be worn.

c. Gloves.

i. When handling hazardous chemicals or contacting potentially contaminated surfaces, protective gloves are to be worn.

ii. Wear gloves to prevent skin exposure. In a glove box, use the gloves and sleeves. If this chemical is handled in a closed system in a certified chemical fume hood, use appropriate chemical-resistant gloves.

NOTE: Consult with your preferred glove manufacturer to ensure that your gloves are compatible with the specific hazardous material.

Refer to glove selection chart from the links below:

http://www.allsafetyproducts.biz/page/74172;

Or

http://www.showabestglove.com/site/default.aspx;

Or

http://www.mapaglove.com/

- iii. Never re-use disposable gloves, such as nitrile or latex.
- iv. If there is a risk of explosion, Kevlar gloves must be worn.
- d. Closed toed shoes.
- e. Covered legs.

Additional PPE may be required if procedures or processes present additional risk. It is the responsibility of the PI to ensure that any additional PPE requirements are identified and communicated to research staff. Contact EH&S for consultation.

3. Hygiene Measures

Avoid contact with skin, eyes and clothing. Wash your hands before breaks and immediately after handling the product.

4. SPECIAL HANDLING PROCEDURES AND STORAGE REQUIREMENTS

Below, a distinction is made between portable, relatively light-weight "lecture bottle" cylinders, and large gas cylinders ("cylinders") that pose additional hazards resulting owing to the weight of the cylinders and the potential for toppling leading to gas discharge.

All transport of toxic gases between on-campus locations must be conducted as follows:

• Gas cylinders must be secured to the transport vehicle (cart, motor vehicle, hand truck, etc.).

- Cylinders must be continuously attended to during transport.
- Cylinders must be clearly labeled with content and hazard information.
- Cylinder caps must be in place.

• Lecture bottles must be secured to a stable surface.

These requirements apply to all listed toxic gas containers, including empty and partially full cylinders.

Upon receipt of toxic gases, cylinders shall be temporarily stored in a well-ventilated area that is attended to or locked at all times. All cylinders shall be immediately leak tested with a leak indicating solution and must be clearly labeled with content and hazard information. Temporary storage locations shall have appropriate signage in place. Cylinders must be seismically secured at all locations with chains at two contact points on the cylinder body, using wall brackets, or an equivalent approved anchoring device. Seismic securing should prevent cylinders from rolling, shifting, or falling.

Laboratory storage of all toxic gas cylinders and lecture bottles shall be in a mechanically ventilated, lockable area. Examples of mechanical ventilation include vented gas cabinets and fume hoods. Rooms containing toxic gases shall be locked when not occupied by authorized persons. All cylinders, lecture bottles, and gas cabinets must be clearly labeled with content and hazard information. Cylinders shall be seismically secured at all locations with chains (two contact points), using wall brackets or an equivalent approved anchoring device for cylinders larger than lecture bottles. Outdoor storage is only allowed on a short term basis in a secure area at least 75 feet from an exterior door, window, or air intake location.

All regulators, valves, and lines must be chemically compatible with the gases being used. Compatibility can be determined by contacting the gas vendor or by calling EH&S. Regulator/line systems must be leak tested immediately after assembly and before each use. Regulators shall be compatible with the size and type of gas cylinder being used, and rated for full cylinder pressure.

All toxic gas cylinders, lecture bottles, and reaction vessels/chambers shall be kept in ventilated enclosures during use and storage. Air-flow velocities at all openings in the vented enclosures must be 0.5 m/s (100 fpm) or greater while in the open position. Where regular access is needed, small access doors must be used to minimize exhaust flow reduction.

All lines or ducts carrying purged or exhausted emissions of toxic gases must be connected to a mechanical exhaust system that discharges to a safe location (i.e., presents no potential for re-entrainment into any building supply air intake or occupied area). Exhaust duct walls shall be chemically resistant to degradation by the toxic gas in use.

Significant emissions of corrosive or toxic gases require an emission control device (e.g., scrubber, flare device, adsorbent) before the purged gas can be vented into the exhaust duct system. Significant emissions are defined as duct concentrations that result in duct corrosion or acute health risk to persons exposed near exhaust fan stacks as determined by release modeling. When toxic gases are emitted from exhaust systems at concentrations which could pose health risks to rooftop workers, locked gates, doors, or other means shall be used to prevent worker access to stack discharge areas. Warning signs must be conspicuously placed.

The following administrative controls must be followed:

1. Never work alone. At least one other person must be present in the same laboratory when any work involving acutely toxic gases is carried out.

2. Eliminate or substitute a less hazardous material when possible.

3. Design your experiment to use the least amount of material possible to achieve the desired result.

4. Verify your experimental set-up and procedure prior to use.

5. Inform your colleagues that this material will be used and where. Label the work area with a sign saying "Acutely Toxic Gas Use Area."

6. Only use if the area is properly equipped with a certified eye wash/safety shower within ten seconds of travel.

7. Consult with the campus Chemical Hygiene Officer if work involves large quantities.

STORAGE:

It is essential that all acutely toxic gases be stored separately from all chemicals with which they may react. Ensure segregation of incompatible chemicals per guidance within the UCI Chemical Hygiene Plan. Also, follow any substance-specific storage guidance provided in Safety Data Sheet (SDS) documentation.

5. SPILL AND INCIDENT PROCEDURES

Indicate how spills or incidents should be handled and by whom (See SafetyNet 13).

If there is an unusual or unexpected occurrence when using this material(s), the occurrence must be documented and discussed with the Principal Investigator or Lab Supervisor and others who might be using the material(s). Unusual or unexpected occurrences might include a fire, explosion, sudden rise or drop in temperature, increased rate of gas evolution, color change, phase change, or separation into layers.

Emergency procedure for leaking gas cylinders:

http://www.airproducts.com/~/media/Files/PDF/company/safetygram-11.pdf

Medical Emergency Dial 911 and EH&S (530) 752-1493

Life-Threatening Emergency, After Hours, Weekends And Holidays – Dial **911.** CALL 911 if the condition is LIFE THREATENING or REQUIRES IMMEDIATE MEDICAL ATTENTION. *Note: All serious injuries <u>must</u> be reported to EH&S at x46200 within 8 <i>hours.* Complete online incident report at <u>https://www.ehs.uci.edu/apps/hr/index.jsp</u>

Non-Life Threatening Emergency – Notify your supervisor or faculty staff if condition is not life threatening.

6. WASTE DISPOSAL

All empty toxic gas cylinders and lecture bottles must be labeled as empty. Ideally, depleted toxic gas cylinders and lecture bottles should be returnable to the vendor according to their guidelines. The purchase of any gases that will not be completely used in the course of research must be approved by the vendor for return, or by EH&S for disposal as hazardous waste. Disposal of toxic gas cylinders and lecture bottles by EH&S, even when empty, may entail extraordinary costs. Therefore, it is recommended that toxic gases should be purchased from vendors who will accept returns.

All waste must be disposed through the EH&S Hazardous Waste Program.

Label all waste with the chemical contents and the appropriate hazard warning.

General hazardous waste disposal guidelines:

All reactive waste **must** be completely quenched before disposal.

Label Waste

• Hazardous waste labels must be affixed to the hazardous waste container upon the start of accumulation. Labels are available online at www.ehs.uci.edu/programs/enviro/.

Store Waste

- Hazardous waste containers must be kept closed, except when adding waste.
- Hazardous waste containers must be stored in secondary containment to adequately contain all of the contents of the container.
- Hazardous waste containers must be inspected weekly for signs of leaks, corrosion, or deterioration.

Dispose of Waste

- Hazardous waste must be transferred to EH&S for disposal within 6 months of being generated.
- Empty Containers: At no time should full or partially full containers be placed in the trash. For more information on empty container management visit http://www.ehs.uci.edu/programs/enviro/.
- Hazardous Waste Disposal:
 - Visit <u>www.ehs.uci.edu/programs/enviro/</u>.
 - Fill out the "Chemical Waste Collection" form.
 - EH&S will pick up your waste within 1-3 days.
- Do not dispose of chemicals by pouring them down the drain or placing them in the trash.
- Do not use fume hoods to evaporate chemicals.

7. PRIOR APPROVAL/REVIEW REQUIRED

All work with Acutely Toxic Gases requires the following prior to beginning work:

1. Must be pre-approved by the Principal Investigator prior to use, and all training must be well documented.

2. Must be familiar with the UCI Chemical Hygiene Plan.

3. Must have documented Chemical and Laboratory Safety training, and specific training on the techniques and processes to be used.

4. Must read the relevant Safety Data Sheet (formerly referenced as Material Safety Data Sheets).

5. Must review the Center for Disease Control, National Institute for Occupational Safety and Health (NIOSH) website - <u>http://www.cdc.gov/niosh/</u> for any relevant information on the material you plan on using.

6. Must read Prudent Practices in the Laboratory: Handling and Management of Chemical Hazards, Updated Edition (2011) section 4.C.2.1 Acute Toxicants and section 7.D Working with Compressed Gases. The following are links to electronic versions of the older edition of this valuable resource: http://www.nap.edu/openbook.php?record_id=4911&page=41#p200063c99970041003 http://www.nap.edu/openbook.php?record_id=4911&page=121 - p200063c99970121002

7. Must follow SafetyNet #60, Compressed Gas Safety (<u>http://safetyservices.ucdavis.edu/safetynets/snml/sn60/sn60</u>).

8. Must demonstrate competence to perform work.

When there are any changes to procedures, personnel, equipment, or when and incident or near miss occurs, a review of this SOP and reapproval is required.

8. DECONTAMINATION

Personnel: Wash hands and arms with soap and water immediately after handling highly toxic gases.

9. DESIGNATED AREA

A designated area shall be established where limited access, special procedures, knowledge, and work skills are required. A designated area can be the entire laboratory, a specific laboratory workbench, or a laboratory hood.

Designated areas must be clearly marked with signs that identify the chemical hazard and include an appropriate warning; for example: WARNING! ACUTELY TOXIC GAS WORK AREA!

10. SAFETY DATA SHEETS AND OTHER RESOURCES

Online SDS can be accessed at http://www.ehs.uci.edu/msds.html.

11. DETAILED PROTOCOL

All lab workers who will be using this material(s) must review this SOP and sign the associated training sheet. Lab workers must have specific training on the proper handling of this material(s) and understand the hazards.

Lab workers using this material(s) must demonstrate competence to the Principal Investigator or designee by being able to:

1) identify the hazards and list any particularly hazardous handling techniques (use of a Schlenck line, rotary evaporation, cannula transfer, extremes of pressure or temperature, etc.);

- 2) list the foreseeable emergency situations;
- 3) describe the proper response to the emergency situations;
- 4) know the control measures to minimize the risks.

When working in the lab using toxic gases, a laboratory worker must:

- (1) <u>never</u> work alone,
- (2) notify all nearby co-workers and the PI (or designee) that toxic gases will be used,
- (3) be cognizant of all the SDS and safety information presented in this document,

(4) find/follow a literature experimental procedure describing the use of the reagent(s) covered by this SOP in a related chemical transformation. If a pertinent literature

protocol cannot be found, the researcher MUST discuss the planned experiment with the PI (or designee) prior to using the reagent,

(5) not deviate from the literature experimental protocol mentioned in (3) in either temperature or pressure without PRIOR APPROVAL from the PI (or designee),

(6) follow all related SOPs in the laboratory SOP bank (PPE, syringe techniques, waste disposal, etc. as appropriately modified by any specific information in the SDS information presented in this document),

(7) the use of large quantities of reagent (>100 mmol) REQUIRES the approval of PI or designee), and

(8) discuss ALL issues or concerns regarding this reagent with the PI prior to its use.

Lab-Specific Operating Procedures

The acutely toxic gases covered by this document include corrosive gases, oxidants, and those with general systemic toxicity. Handling of each of these different types of toxic gases should be done according to the following general instructions, with specific class-specific details found below.

General:

- 1. Safely secure gas cylinder with chains (two contact points), wall brackets, or other approved anchoring device. For lecture bottles, secure with chain clamp or ring clamp to solid structure in the work area.
- 2. Unscrew and remove cap from large gas cylinder.
- 3. Ensure main valve is completely closed.
- 4. Unscrew and remove main valve cap, if present.
- 5. Attach appropriate pressure regulator and connect tubing from regulator to reaction vessel, which must be placed in a well-ventilated fume hood with sash closed as much as reasonably possible.
- 6. Ensure that all fittings are secure. Have another experienced laboratory member or PI check apparatus setup before proceeding.
- 7. Dispense gas into reaction vessel by slowly opening main valve, using appropriate pressure, flow rate, and exhaust/scrubbing system, and taking into account detailed instructions for specific classes below.
- 8. Turn off main valve, and remove tubing from the reaction vessel.
- 9. Once the reaction is complete, purge the vessel with inert gas (nitrogen or argon) with appropriate scrubbing of excess gas.
- 10. Slowly release residual pressurized gas from the regulator with appropriate scrubbing.
- 11. Remove regulator from tank and allow to vent in fume hood.
- 12. Replace and secure main valve cap and cylinder cap.

- I. Commonly encountered corrosive gases (e.g. gaseous hydrogen fluoride, hydrogen chloride, hydrogen bromide, hydrogen sulfide, ammonia, boron trichloride, boron trifluoride): These agents are either strongly acidic or basic, and any exhaust of these gases must be neutralized with an appropriate scrubbing apparatus. For acidic gases (hydrogen fluoride, hydrogen chloride, hydrogen bromide, hydrogen sulfide), the vessel can be vented via tubing into an excess of a solution of cold aqueous 1 M sodium hydroxide. Scrubbing solutions used for hydrogen sulfide must be kept basic and labeled for separate disposal to avoid accidental acidification and re-release of this toxic gas. For basic gases (e.g. ammonia), the scrubbing solution should consist of an excess of cold aqueous 1 M hydrochloric acid. Because boron trichloride and boron trifluoride react violently with water, dilution is recommended prior to decomposition with aqueous base. For significant quantities, dilute with THF or 1,4-dioxane and add slowly dropwise to a stirred solution of ice-chilled dilute aqueous NaOH.
- II. Strongly oxidizing gases (e. g. chlorine, fluorine): These agents must be neutralized with an appropriate scrubbing apparatus. The vessel can be vented via tubing into an excess of a solution of cold aqueous 1 M sodium bisulfite or sodium thiosulfate.
- III. Gases with general acute toxicity (e. g. arsine, cyanogen, cyanogen chloride, carbon monoxide, methyl mercaptan, hydrogen sulfide, phosgene, phosphine): These gases should be used with minimal excess exhaust. Each of these agents is sufficiently toxic that separate Standard Operating Procedures for each should be in place and must be followed.

For uses of toxic compressed gases to pressurize reaction vessels (for example, in highpressure carbonylation reactions using carbon monoxide), see specific Standard Operating Procedure for that particular gas.

NOTE

Any deviation from this SOP requires approval from PI.

Documentation of Training (signature of all users is required)

- Prior to conducting any work with acutely toxic gases, designated personnel must provide training to his/her laboratory personnel specific to the hazards involved in working with this substance, work area decontamination, and emergency procedures.
- The Principal Investigator must provide his/her laboratory personnel with a copy of this SOP and a copy of the SDS provided by the manufacturer.
- The Principal Investigator must ensure that his/her laboratory personnel have attended appropriate laboratory safety training or refresher training within the last one year.

I have read and understand the content of this SOP:

Name	Signature	Date

APPENDIX:

Acutely Toxic Gases Used in Lab

????

Appendix R: Peroxide-Forming Chemicals SOP

Standard Operating Procedure

Peroxide-Forming Chemicals

Department:	????
Date SOP written:	????
Date SOP approved by PI/lab supervisor:	????
Principal Investigator:	????
Internal Lab Safety Coordinator/Manager:	????
Lab Phone:	????
Office Phone:	????
Emergency Contact:	????
Location(s) covered by this SOP:	????

Type of SOP: Difference Process Difference Hazardous Chemical

X Hazardous Class

Purpose

This SOP applies to the various chemicals that can form peroxides. The peroxide forming chemicals should be tested every three to six months to ensure that peroxides have not formed. Various peroxide forming chemicals are listed below.

Divinyl acetylene, Divinyl ether, Isopropyl ether, Potassium amide, Sodium amide, Vinylidene chloride (1,1-dichloroethylene), Potassium, Cyclohexene, Cyclopentene, Decalin, Diacetylene (gas), Dicyclopentadiene, Diethyl ether (ether), Dioxane, Ethylene glycol dimethyl ether (glyme), Furan, Methyl isobutyl ketone, Methyl acetylene (gas), Methyl cyclopentane, Tetrahydrofuran (THF), Tetralin (tetrahydronaphthalene), Acrylic acid, Acrylonitrile, Butadiene, Chlorobutadiene, Chloroprene, Chlorotrifluoroethylene (gas), Methyl methacrylate, Styrene, Tetrafluoroethylene (gas), Vinyl acetate, Vinyl acetylene (gas), Vinyl chloride (gas), 4-Vinylpyridine, 2-Vinylpyridine, Vinylidene chloride

A list of the peroxide-forming chemicals used in this lab is shown in the Appendix at the end of this document.

Physical & Chemical Properties/Definition of Chemical Group

Depending on the danger of peroxide accumulation, peroxide forming chemicals can be divided into three categories (Class A-C).

Class A: Chemicals that form explosive levels of peroxides without concentration. These are the most hazardous and can form explosive peroxide levels even if not opened. Test for peroxide formation or discard after 3 months of receiving the chemicals.

Isopropyl ether	Divinyl acetylene	Potassium metal
Potassium amide	Sodium amide	Vinylidene chloride

Class B: Chemicals that form explosive levels of peroxides on concentration through distillation, evaporation or exposure to air after opening. Test for peroxide formation or discard after 12 months.

Acetal	Acetaldehyde	Benzyl Alcohol
2-Butanol	Chlorofluoroethylene	Cumene(isopropylbenzene)
Cyclohexene	2-Cyclohexen-1-ol	Cyclopentene
Decahydronapthalene(decalin)	Diacetylene(butadiyne)	Dicyclopentadiene
Diglyme	Diethyl ether	Ethylene glycol ether acetates
Furan	4-Heptanol	2-Hexanol
Methyl Acetylene	3-Methyl-1-butanol	Methyl-isobutyl ketone
4-Methyl-2-pentanol	2-Pentanol	4-Penten-1-ol
1-Phenylethanol	Tetrahydrofuran	Tetrahydronapthalene
Vinyl Ethers	Sec. Alcohols	Dioxanes
Ethylene glycol dimethyl ether (glyme)		

Class C: Chemicals that may autopolymerize as result of peroxide formation. Test for peroxide formation or discard after 12 months.

Acrylic acid	Styrene	Acrylonitrile
Tetrafluoroethylene	Butadiene	Vinyl acetylene
Chloroprene	Vinyl acetate	Chlorotrifluoroethylene
Vinyl chloride	Methyl methacrylate	Vinyl pyridine

Potential Hazards/Toxicity

Physical Hazards

Peroxide forming chemicals are flammable and may form explosive peroxides.

Organic peroxides are organic compounds containing the peroxide functional group (ROOR'). These materials are sensitive to oxygen, heat, friction, impact, light, and strong oxidizing and reducing agents. The unusual stability problems of this class of compounds make them a serious fire and explosion hazard that requires careful management.

HEALTH HAZARDS

Harmful if swallowed. Irritating to eyes and skin. Vapors may cause drowsiness and dizziness. Aspiration hazard if swallowed - can enter lungs and cause damage. May cause irritation of respiratory tract. Repeated exposure may cause skin dryness or cracking.

Specific health hazards may vary per compound. Consult individual compound's SDS.

Personal Protective Equipment (PPE)

Respirator Protection

Respiratory protection is generally not required for lab research, provided the appropriate engineering controls are employed. Respirators should be used only under any of the following circumstances:

Respirators should be used only under any of the following circumstances:

- As a last line of defense (i.e., after engineering and administrative controls have been exhausted).
- When Permissible Exposure Limit (PEL) has exceeded or when there is a possibility that PEL will be exceeded.
- Regulations require the use of a respirator.
- An employer requires the use of a respirator.
- There is potential for harmful exposure due to an atmospheric contaminant (in the absence of PEL)
- As PPE in the event of a chemical spill clean-up process

Lab personnel intending to use/wear a respirator mask must be trained and fit-tested by EH&S. This is a regulatory requirement.

Hand Protection

Handle with gloves. Appropriate disposable nitrile gloves should be worn when dealing with small quantities of peroxide forming chemicals. Lab workers should consult EH&S for appropriate selection of gloves when dealing with chemicals for a prolonged period of time.

NOTE: Consult with your preferred glove manufacturer to ensure that the gloves you plan on using are compatible with specific chemicals.

Refer to glove selection chart from the links below: <u>http://www.ansellpro.com/download/Ansell_8thEditionChemicalResistanceGuide.pdf</u> OR <u>http://www.allsafetyproducts.biz/page/74172</u> OR <u>http://www.showabestglove.com/site/default.aspx</u> OR http://www.mapaglove.com/

Eye Protection

ANSI approved, tight-fitting safety glasses/goggles. Face shields are recommended. Face shields provide protection to the face, not the eyes and should never be worn alone. Face shields should be worn with appropriate safety glasses or goggles.

Skin and Body Protection

Flame resistant lab coat preferably made of antistatic material, long pants, and closed-toe shoes.

Hygiene Measures

Avoid contact with skin, eyes and clothing. Wash hands before breaks and immediately after handling the product.

Engineering Controls

a. Chemical fume hood with adequate exhaust ventilation.

b. Portable explosion shield: May also be required to control the risk of explosion.

c. Use bonding and grounding equipment to minimizing the likelihood of an ignition from static electricity during the transfer of all Class I flammable liquids.

d. Know where your safety equipment is located (i.e., fire extinguisher, eye wash/safety shower, and first aid kit).

e. Have the appropriate fire extinguisher available.

Required Training / Approvals

All work with peroxide forming chemicals requires the following prior to beginning work:

1. Any work with Class A peroxide-forming chemicals must be pre-approved by the Principal Investigator prior to use and all training must be well documented.

2. Must be familiar with the Chemical Hygiene Plan.

3. Must have documented Laboratory Safety Principles/IIPP training.

4. Must follow this SOP.

5. Must read the relevant Safety Data Sheet (formerly referenced as Material Safety Data Sheets).

6. Must read Prudent Practices in the Laboratory: Handling and Management of Chemical Hazards (section 6.G. Working with Highly Reactive or Explosive Chemicals).

7. Any additional laboratory specific training required to support this SOP must be referenced in the Laboratory Specific Instructions section and the signed and dated training documents must be uploaded into each assigned researcher's training records. Examples include Safety Data Sheets, experimental procedures, journal articles, etc.

Administrative Controls

1. <u>Never</u> work alone. At least one other person must be present in the same laboratory when any work involving acetic acid is conducted.

2. Eliminate or substitute for a less hazardous material when possible.

3. Design your experiment to use the least amount of material possible to achieve the desired result.

4. Verify your experimental set-up and procedure prior to use.

5. Inform colleagues this material will be used and where.

6. Only use if the area is properly equipped with a certified eye wash and safety shower within ten seconds of availability.

7. Consult with the PI if work involves large quantities.

First Aid Procedures

Consult the SDS for the compound being used. General first aid procedures for hazardous chemicals typically include:

If inhaled

Move person into fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Seek medical aid immediately.

In case of skin contact

Wash skin with soap and water for at least 15 minutes while removing contaminated clothing and shoes. Wash clothing before reuse. Thoroughly clean shoes before reuse. If frostbite occurs, flush affected areas with lukewarm water. Consult a physician.

In case of eye contact

Flush eyes with plenty of water for at least 15 minutes. Consult a physician.

If swallowed

Do NOT induce vomiting unless directed by medical personnel. Never give anything by mouth to an unconscious person. Seek medical attention immediately.

Special Handling and Storage Requirements

Precautions for safe handling: Avoid contact with skin, eyes, and clothing. Avoid inhalation. Avoid heat, flames, sparks, and other sources of ignition- No smoking. Avoid shock or friction. Protect from physical damage. Secure cylinder when using to protect from falling. Use suitable hand truck to move cylinders. **Conditions for safe storage:** Keep container tightly closed in a cool, dry, and well-ventilated area. Keep valve protection cap on cylinders when not in use. Incompatible with oxidizing agents, halogens, copper, and copper alloys. Do not store with strong oxidizing or strong reducing agents. Do not store with incompatible materials. Refer to SDS for additional storage requirements per individual compound. Test for peroxide formation or discard every three months for Class A compounds and annually for Class B and C compounds.

Spill and Accident Procedure

Chemical Spill Dial 911

Spill – Assess the extent of danger. Help contaminated or injured persons. Turn off all sources of ignition. Ventilate potentially explosive atmospheres. If possible without risk, stop flow of gas. If source of leak is a cylinder and cannot be stopped, remove cylinder to a safe place in the open air. Repair leak or allow cylinder to empty. If leak is in liquid form, allow to evaporate. Evacuate the spill area. Close all doors to confine spill in a properly ventilated area. Avoid breathing vapors. Keep others from entering contaminated area (e.g., use caution tape, barriers, etc.). Clean-up personnel should wear fully-encapsulating, vapor- protective clothing and equipment.

Dial 911 and EH&S at x 46200 for assistance.

Chemical Spill on Body or Clothes – Remove clothing and rinse body thoroughly in emergency shower for at least 15 minutes. Seek medical attention. *Notify immediately the supervisor and EH&S at x46200.*

Chemical Splash Into Eyes – Immediately rinse eyeball and inner surface of eyelid with water from the emergency eyewash station for 15 minutes by forcibly holding the eye open. Seek medical attention. *Notify immediately the supervisor and EH&S at x46200.*

Article V. Medical Emergency Dial 911

a. Life Threatening Emergency, Business Hours, After Hours, Weekends and Holidays – Dial 911 CALL 911 if the condition is LIFE THREATENING or REQUIRES IMMEDIATE MEDICAL ATTENTION.. <u>Note</u>: All serious injuries <u>must</u> be reported to EH&S at x46200 within 8 hours. Complete online incident report at <u>https://www.ehs.uci.edu/apps/hr/index.jsp</u>

b. Non-Life Threatening Emergency – Notify your supervisor or faculty staff if condition is not life threatening.

c. Needle Stick/puncture Exposure (as applicable to chemical handling procedure) – Wash the affected area with antiseptic soap and warm water for 15 minutes. <u>For mucous</u> <u>membrane exposure</u>, flush the affected area for 15 minutes using an eyewash station.

ALL WORK RELATED INJURIES MUST BE REPORTED via the On-line Incident Form <u>https://www.ehs.uci.edu/apps/hr/index.jsp</u> or call Human Resources, Workers Compensation (949) 824-9152.

Decontamination/Waste Disposal Procedure

Wearing proper PPE, decontaminate equipment and bench tops using soap and water. Dispose of the used chemical and contaminated disposables as hazardous waste following the guidelines below.

General hazardous waste disposal guidelines:

Label Waste

• Hazardous waste labels must be placed on the hazardous waste container upon the start of accumulation. Labels are available online at www.ehs.uci.edu/programs/enviro/.

Store Waste

- Hazardous waste containers must be kept closed, except when adding waste.
- Hazardous waste containers must be stored in secondary containment to adequately contain all of the contents of the container.
- Hazardous waste containers must be inspected weekly for signs of leaks, corrosion, or deterioration.

Dispose of Waste

- Hazardous waste must be transferred to EH&S for disposal within 6 months of being generated.
- Empty Containers: At no time should full or partially full containers be placed in the trash. For more information on empty container management visit www.ehs.uci.edu/programs/enviro/.
- Hazardous Waste Disposal:
 - Visit <u>www.ehs.uci.edu/programs/enviro/</u>.
 - Fill out the "Chemical Waste Collection" form.
 - EH&S will pick up your waste within 1-3 days.
- Do not dispose of chemicals by pouring them down the drain or placing them in the trash.
- Do not use fume hoods to evaporate chemicals.

Safety Data Sheet (SDS) Location

Online SDS can be accessed at http://www.ehs.uci.edu/msds.html.

Designated Area

Peroxide-forming chemicals (such as tetrahydrofuran) are worked with throughout the entire laboratory.

Prior Approval Required

All work with peroxide forming chemicals requires the following prior to beginning work:

1. Must be familiar with the UC Irvine Chemical Hygiene Plan. See <u>http://www.ehs.uci.edu/programs/lsg/TABLEofCONTENTS.pdf#page=069</u>

2. Must have documented Laboratory Safety training.

3. Must read the relevant Safety Data Sheet (formerly referenced as Material Safety Data Sheets).

Lab-Specific Procedures

Lab-specific procedures for this class of chemicals include storing, dispensing, use in chemical reactions, use in processes (e.g., distillation, rotary evaporation, or chromatography), and disposal. Appropriate personal protective equipment and engineering controls are to be used.

Detection of Peroxides

Before distilling or purifying any known or suspected peroxide-former, check it carefully for the presence of peroxides. Peroxide crystals tend to form on the inner surfaces of the container. If you do see viscous liquid or crystalline solids, do not handle the chemical any further. The crystals may cause an explosion if subjected to impact or friction. Contact EHS at 46200 for the peroxides removal and disposal. If you do not see crystals, or if the container is metal or opaque, proceed to the following tests. Either of the following tests will detect most (but not all) peroxy compounds including all hydroperoxides:

- 1. Add 1-3 ml of the liquid to be tested to an equal volume of acetic acid, add a few drops of 5% aqueous KI solution, and shake. The appearance of a yellow to brown color indicates the presence of peroxides.
- 2. Add 0.5 ml of the liquid to be tested to a mixture of 1 ml of 10% aqueous KI solution and 0.5 ml of dilute HCl to which has been added a few drops of starch solution just prior to the test. The appearance of a blue or blue-black color within a minute indicates the presence of peroxides.
- 3. The easiest method of detecting peroxides in common solvents is to use peroxide test strips that are semi-quantitative and give readings in the range from 0 25 ppm. Contact EHS for guidance on obtaining test strips.

Test Results:

>03-30 parts per million (ppm) - Expired compounds testing within this range offer little or no threat of violent reaction on the given test date. For compounds testing in this range, the investigator should consider the addition of fresh inhibitor to retard the auto-oxidation process and the container should be tightly sealed to prevent air and light exposure.

>30 and <80 ppm - Expired or mismanaged compounds originally inhibited by the supplier which test within this range may well be on the way to posing a threat to the operations of the laboratory. Several documented major exothermic reactions have occurred during the reduction of peroxides in drums, bottles, cans and laboratory ware within this range.

>80 ppm - Any suspect container testing in excess of the limits of standard peroxide test strips must be considered to be potentially shock sensitive. High peroxide concentrations may occur without the presence of visible crystals.

Storage of Peroxide Forming Chemicals

General Precautions

Minimize the quantity of peroxides or peroxide forming chemicals in the lab.

Label each container with the Date Received, Date Opened and Date Last Tested.

Segregate these compounds from incompatible materials. Store away from ignition sources. Protect from flames, static electricity, and sources of heat.

Test chemicals for peroxide before any distillation or purification of peroxide forming chemicals.

Use extreme caution before concentrating or purifying peroxide forming chemicals as most explosions occur during these processes.

Wear proper personal protective equipment, including safety eyewear and face shields, when working with peroxide forming chemicals.

Minimize peroxide formation in ethers by storing in tightly sealed containers in a cool place in the absence of light.

If solids or crystals are observed in either the liquid or around the cap of peroxide forming chemicals, do not open or move the container but contact EHS for disposal.

Storage Limits for Each Class of Peroxide Forming Chemicals

<u>Class A.</u> Storage Unopened: six (6) months maximum. Storage Opened: test upon opening. If the test indicates > 80 ppm peroxides dispose. If < 80 ppm peroxide retest every 3 months and dispose when the test indicates > 80 ppm peroxides, the manufacturer expiration date is reached or one year from the date of receipt whichever occurs first.

<u>Class B</u>. Storage Unopened: one (1) year maximum. Storage Opened: test upon opening. If the test indicates > 80 ppm peroxides dispose. If < 80 ppm peroxide retest every 3 months and dispose when the test indicates > 80 ppm peroxides or the manufacturers expiration date is reached whichever occurs first.

<u>Class C</u>. Storage Unopened: one (1) year maximum. Storage Opened: test upon opening. If the test indicates > 80 ppm peroxides dispose. If < 80 ppm peroxide retest every 3 months and dispose when the test indicates > 80 ppm peroxides or the manufacturers expiration date is reached whichever occurs first.

Handling Peroxide Forming Chemicals

Safety Precautions: Personnel handling containers of outdated peroxide-forming chemicals must wear chemical goggles and a face shield, heavy gloves, and a buttoned lab coat. Hearing protection (plugs or muffs) and a rubber apron are also recommended. Suspect chemical containers must be transferred, one at a time, to a clean (no other chemicals) lab hood. A blast shield must be used when opening or manipulating containers, and testing peroxide levels. Never attempt to force open a stuck cap on a container. NEVER scrape or scrub glassware or containers that have been used with peroxide-forming compounds if you see an oily or crusty residue. Secondary containment for the chemical should also be utilized if practical. Tongs or other forms of remote handling should be used as much as practical. Verify that an operable safety shower/eyewash and fire extinguisher is readily accessible. At least one other person not directly involved in handling of the chemicals must be present.

Visual Inspection: Visually inspect all peroxide-forming chemicals before any further operation. Containers that exhibit any unusual visual characteristics, such as the examples listed below, should be assumed to contain dangerous levels of peroxides and must not be disturbed. Notify EH&S, who will assist in the further evaluation. If there is any doubt about the safety of handling a chemical container, notify EH&S immediately.

<u>For liquid chemicals</u>, look for crystallization (around the cap or in the liquid), visible discoloration, and liquid stratification. Diethyl ether is commonly sold in steel containers which prevents visual inspection of the liquid. Therefore, diethyl ether containers whose age and use history are unknown should be assumed to contain dangerous levels of peroxides and should not be disturbed.

<u>For Solid Chemicals</u> (potassium metal, potassium and sodium amide), look for discoloration and/or formation of a surface crust (for example, potassium metal forms a yellow or orange superoxide at the surface). Evaluation of alkali metals and their amides is based on visual criteria only. These substances react strongly with water and oxygen, and the standard operation procedure of pyrophoric compounds should be followed for these chemicals.

Materials meeting the above criteria are considered to be high risk and will have to be disposed of by special means (limit handling and movement; notify EH&S at x46200). Only chemicals that pass visual inspection should be evaluated further.

Opening Container (Note: Never try to force open a rusted or stuck cap on a container of a peroxide-forming chemical.)

a. Only chemicals that meet the below criteria should be opened and tested for peroxides. Chemicals that do not meet one or more of these criteria should be considered to be high risk, and should not be disturbed. Limit handling and movement; notify EH&S at x46200.

- The identity of the chemical is known.
- The age of the chemical (since manufacture) is known.

Evaporation of the chemical is thought to be less than 10% - if this is in question, assume that evaporation has occurred and that high peroxide levels may be present.

b. Additionally, the following classification-specific criteria must be met:

• Previously opened chemicals not used in the preceding 3 months must be less than 6 months old.

List A Chemicals

• Chemicals unopened from the manufacturer must be less than 1 years old. If this is in question, assume the container has been opened.

• Opened chemicals not used in the preceding 3 months must be less than 1 years old.

List B and List C (liquids) Chemicals

• Chemicals unopened from the manufacturer must be less than 1 years old. If this is in question, assume the container has been opened.

Chemicals not meeting the minimum criteria for opening and testing will be considered to be high risk and must be disposed of by special means. Limit handling and movement; notify EH&S x46200. If after opening the container, visual irregularities such as those listed in section 1 are apparent, assume that dangerous levels of peroxides are present. Gently cover the container to minimize evaporation, limit handling and movement, and notify EH&S x46200 as soon as possible.

Distillation. NEVER distill potential peroxide-forming chemicals to dryness. Always leave a minimum of 20% still bottoms. When possible, adding a non-volatile organic compound (such as mineral oil) can dilute the peroxides remaining after distillation. When preparing to distill or evaporate peroxide forming chemicals, always test for peroxides first.

Stabilization of Peroxides

Even if the concentration of peroxides is less than 0.001% (10 ppm), you should periodically stabilize your chemical from additional formation of peroxides if feasible. To do so, add at least 1 gram of butylated hydroxytoluene (BHT) per liter of chemical. BHT is an antioxidant that slows the oxidation of peroxide forming chemicals. BHT will not destroy peroxides already present. Once you have stabilized the chemical, label the substance with the peroxide concentration and indicate the date that you stabilized it. Store the substance properly or manage as hazardous waste.

Disposal of Peroxide Forming Chemicals

1. Contact EHS at x46200 for disposal of peroxide forming chemicals.

2. Chemicals with a peroxide concentration greater than 800 ppm are considered high risk, and require disposal by special means. DO NOT attempt to decrease peroxide concentration. Limit handling and movement of the chemical container. Notify EH&S.

NOTE

Any deviation from this SOP requires approval from PI.

Documentation of Training (signature of all users is required)

- Prior to conducting any work with peroxide forming chemicals, designated personnel must provide training to his/her laboratory personnel specific to the hazards involved in working with this substance, work area decontamination, and emergency procedures.
- The Principal Investigator must provide his/her laboratory personnel with a copy of this SOP and a copy of the SDS provided by the manufacturer.
- The Principal Investigator must ensure that his/her laboratory personnel have attended appropriate laboratory safety training or refresher training within the last one year.

I have read and understand the content of this SOP:

Name	Signature	Date

APPENDIX:

Peroxide-Forming Chemicals Used in Lab

????

Appendix S: Potentially Explosive Chemicals SOP

Potentially Explosive Compounds	
Department:	????
Date SOP written:	????
Date SOP approved by PI/lab supervisor:	????
Principal Investigator:	????
Internal Lab Safety Coordinator/Manager:	????
Lab Phone:	????
Office Phone:	????
Emergency Contact:	????
Location(s) covered by this SOP:	????

Standard Operating Procedure

Type of SOP:
□ Process□ Hazardous ChemicalX Hazardous Class

Purpose

The purpose of this standard operating procedure is to acquaint you with potentially explosive chemicals, the common triggers of explosions, and safety practices. Above all, use a combination of common sense and chemical sense.

A list of the potentially explosive chemicals used in this lab is shown in the Appendix at the end of this document.

Chemical classes of explosives - According to *Prudent Practices in the Laboratory: Handling and Management of Chemical Hazards* (section 4.D.3.1 Explosive Hazards) The National Academies Press: Washington, DC, 2011.

"An explosive is any chemical compound or mechanical mixture that, when subjected to heat, impact, friction, detonation, or other suitable initiation, undergoes rapid chemical change, evolving large volumes of highly heated gases – typically nitrogen or CO_2 – that exert pressure on the surrounding medium. The term applies to materials that either detonate or deflagrate."

All compounds with bonds between electronegative atoms should be considered to be highly reactive, but the following functional groups should alert you to danger: peroxides (-O-O-, -O-O-, -O-), nitro compounds (O-NO₂, N-NO₂, and C-NO₂), nitroso compounds (O-NO, N-NO), azo and related compounds ($C=N_2$, $R-N_2^+$, -N=N-, $-N_3$, -N=N-S-N=N-), hypohalites and haloamines (RCOO-X, N-X), oxyhalide salts (ClO₄-, ClO₃-, BrO₃-, IO₃-, ClO₂, ClO-) and related metal salts (M-N₃, M-CC-M, M-N=C=O, M-OCIO₃, picrates, dinitrophenolates).

Chemical factors that affect stability - Note that the explosive potential of any substance depends on several factors:

1. **Dilution**: Pure solids and pure liquids are much more dangerous than solutions. *Dilution reduces the potential for explosive chain reactions.*

2. **Functional group density** - The explosive hazard is increased when unstable functional groups make up most of the organic molecule. Trinitrotoluene is dangerous whereas nitrotoluene is not. Remember the azide rule: NEVER attempt to isolate an organic azide with a carbon-to-nitrogen ratio of less than 1.

Triggers - There are a variety of common triggers for chemical explosions: heat, impact, friction, catalysts, and even light.

• Heat facilitates explosive detonations. Store potentially dangerous compounds at low temperature. See your PI before heating any reaction that involves potentially explosive compounds.

• Shock-sensitive materials include metal acetylides, azides, nitrogen triiodide, nitrate esters, nitro compounds, metal perchlorates, many organic peroxides, and compounds containing diazo, halamine, nitroso, and ozonide functional groups.

• Many metal ions, including the iron in rust, can catalyze the violent decomposition of peroxides.

• Acids, bases, and other substances catalyze the explosive polymerization of acrolein. Hydrogen and chlorine react explosively in the presence of light.

Think ahead: Before you work with potentially explosive chemicals inform your PI; then review the relevant Material Safety Data Sheet and appropriate chemical safety resources. Review specific procedures for emergency response, chemical exposure, or injury to staff, including any special first aid measures. Above all, anticipate explosions before they occur and <u>use common sense</u>! ALWAYS wear protective eyewear; work with the hood sash closed; use a blast shield.

If you have questions concerning the applicability of any item listed in this procedure see your PI or EH&S. Prudent Practices in the Laboratory: Handling and Management of Chemical Hazards (section 4.D.3.1 "Explosive Hazards" and also section 6.G., "Working with highly reactive or explosive chemicals." In *Prudent Practices in the Laboratory: Handling and Management of Chemical Hazards*. The National Academies Press: Washington, DC, 2011.

Get Permission: Attention! Federally regulated explosives are strictly controlled. Please refer to the most recent list from the Bureau of Alcohol, Tobacco, and Firearms to see if the material you

are interested in buying or making a compound that is on their list: <u>http://www.atf.gov/regulations-rulings/rulemakings/general-notices.html</u>. There are over 200 compounds and compound classes on the ATF list, including some surprisingly common reagents like dinitrophenylhydrazine. If you want to purchase or synthesize any of the explosives on the ATF list you must first contact EH&S. No exceptions!

Definition of Chemical Group

The following compounds and compound classes are considered explosive:

Potentially Explosive Compounds: Acetyl peroxide, Acetylene, Ammonium nitrate, Ammonium perchlorate, Ammonium picrate, Benzoyl peroxide, Bromopropyne, Butanone peroxide, Cumene peroxide, Diazodinitrophenol, Dinitrophenol, Dinitrophenylhydrazine, Dipicryl amine, 2,4-Dinitroresorcinol, 4,6-Dinitroresorcinol, Dipicryl sulphide, Dodecanoylperoxide, Ethylene oxide, Lauric peroxide, MEK peroxide, Silver fulminate, Mercury fulminate, Nitrogen trifluoride, Nitrocellulose, Nitrogen triiodide, Nitroglycerin, Nitroguanidine, Nitromethane, Nitrourea, Picramide, Picric acid (trinitrophenol), Picryl chloride, Picryl sulphonic acid (trinitrobenzenesulphonic acid), Propargyl bromide (neat), Sodium dinitrophenolate, Sodium dinitrophenolate, Succinic peroxide, Tetranitroaniline, Trinitroaniline, Trinitroanisole, Trinitrobenzene, Trinitrobenzoic acid, Trinitrocresol, Trinitronaphthalene, Trinitronaphthalene, Trinitronaphthalene, Trinitroresorcinol, Trinitrotoluene, Urea nitrate

Potentially Explosive Classes of Chemicals: Metal Acetylides (M-C=C-), Acyl hypohalites (RCO-OX), Organic Azides (R-N₃), Metal azides (M-N₃), Azo (-N=N-), Diazo (=N=N), Diazosulphide (-N=N-S-N=N-), Diazonium salts (R-N₂+), Fulminate (-CNO), Halogen Amine (=N-X), Nitrate (-ONO₂), Nitro (-NO₂), Aromatic or Aliphatic Nitramine (=N-NO₂) (-NH-NO₂), Nitrite (-ONO), Nitroso (-NO), Ozonides, Peracids (-CO-O-O-H), Peroxide (-O-O-), Hydroperoxide (-O-O-H), Metal peroxide (M-O-O-M), Bromate salts (BrO₃-), Chlorate salts (CIO₃-), Chlorate salts (CIO₂-), Perchlorate salts (CIO₄-), Picrate salts (2,4,6-trinitrophenoxide), Picramate salts (2-amino-4,6-dinitrophenoxide), Hypohalite salts (XO-), Iodate salts (IO₃-).

Use chemical sense: Anticipate the formation of potentially explosive intermediates like peroxides or azides in your chemical reactions, even if you have no intention of isolating them. In such cases, take appropriate precautions.

Potential Hazards – Lacerations, Burns, Contamination

The danger of explosive compounds arises from lacerations due to shrapnel (metal, glass, ceramic, etc.) and burns due to fires that might accompany or follow the explosion.

An explosion might also lead to exposure to toxic chemicals. See the appropriate SOPs and MSDSs for any other chemicals used in tandem with potentially explosive chemicals.

Personal Protective Equipment (PPE)

Lab personnel are instructed to wear PPE at all times while handling hazardous materials/occupying laboratory areas.

Eye Protection

Safety glasses with side shields will help to protect your eyes from shrapnel. If there is any danger of an explosion while working with compounds outside of a hood, use a face shield (8-inch minimum). Use equipment for eye protection tested and approved under appropriate government standards such as NIOSH (US) or EN 166(EU).

Skin and Body Protection

Long pants and a lab coat will provide additional protection against lacerations. Closed toed and closed heeled shoes, cotton-based clothing/attire, and flame resistant lab coat must be worn.

Hand Protection

Choose gloves that provide a balance between protection against lacerations (in case of an explosion) and the agility needed to work nimbly with potentially explosive compounds.

Potentially explosive compounds may also be toxic. See the MSDS for every compound you work with and the SOP for toxic compounds. Inspect gloves prior to use. Dispose of contaminated gloves after use in accordance with applicable laws and good laboratory practices. Wash and dry hands.

Engineering Controls

Fume Hood

Reactions involving potentially explosive reagents, intermediates, or products should be conducted in a hood with the sash closed. The fume hood is made of metal and safety glass and is your main protection from explosions. In the case of violent explosions the safety glass will shatter and blow out from the hood. Don't linger in front of your hood if it contains an explosive compound, or even if you suspect it.

Portable Blast Shield

When working with potentially explosive compounds the use of the portable blast shield, inside the hood, is recommended. Our blast shield is made of impact-resistant plastic and can provide three-sided protection and it also allows you to see what is going on in your reaction. Put the blast shield between the reaction vessel and the closed hood sash.

Required Training / Approvals

All work with these materials requires the following prior to beginning work:

- 1. Must be pre-approved by the Principal Investigator prior to use and all training must be well documented.
- 2. Must be familiar with the Chemical Hygiene Plan.
- 3. Must have documented Laboratory Safety Principles/IIPP (SOS) training.
- 4. Must follow this SOP.
- 5. Must read the relevant Safety Data Sheet (formerly referenced as Material Safety Data Sheets).
- 6. Must read Prudent Practices in the Laboratory: Chapter 4 "Evaluating Hazards and

Assessing Risks in the Laboratory" -<u>http://www.nap.edu/openbook.php?record_id=12654&page=45</u> and Chapter 6 "Working with Chemicals" <u>http://www.nap.edu/openbook.php?record_id=12654&page=105</u> 7. All work involving energetic materials (explosives):

- - Must be pre-approved by the PI and the Campus Fire Marshal.
 Must develop an energetic material / explosives safety plan
 - Must establish a qualification /certification plan for users
 - Must demonstrate proficiency
 - PI must set limits on not to exceed quantity of energetic material

- Must review the Chemical Safety Board report on explosives safety: <u>http://www.depts.ttu.edu/vpr/integrity/csb-response/downloads/report.pdf</u>
- 8. Any additional laboratory specific training that is needed to support this SOP must be referenced in the 'Laboratory Specific Instructions' section and the signed and dated training documents must be uploaded into each assigned researchers training records. Examples include Safety Data Sheets, experimental procedures, journal articles, etc.

Administrative Controls

- 1. Never work alone.
- 2. Eliminate or substitute for a less hazardous material when possible.
- 3. Design your experiment to use the least amount of material possible to achieve the desired result.
- 4. Verify your experimental set-up and procedure prior to use.
- 5. Ensure all equipment is appropriate for the task.
- 6. Inform colleagues that this material will be used and where.
- 7. Only use if the area is properly equipped with a certified eye wash/safety shower within ten seconds of travel.
- 8. Ensure that all use details are recorded in a log book which notes the date, user, amount used, and current quantity on hand.
- 9. Consult with the PI when scaling up above 50 mmol of potentially explosive compound or reagent.

Response and First Aid Procedures

If an explosion occurs

Check everyone in the area for lacerations or other injuries; a victim may be unaware of injuries due to the shock of the explosion. If emergency response is needed immediately call 9-1-1. In any case, contact your PI and then the Physical Sciences EH&S Coordinator or EH&S office.

An explosion could release hazardous chemicals

- In case of skin contact wash off with soap and plenty of water. Consult a physician.
- In case of eye contact rinse thoroughly with plenty of water for at least 15 minutes and consult a physician.
- If inhaled move the person into fresh air. If not breathing, give artificial respiration. Consult a physician.

Special Handling and Storage Requirements

GENERAL RULE: WORK WITH LESS

Reduce the quantity of potentially explosive compounds that you work with. Buy less; store less; use less. Before you work with potentially explosive compounds, discuss alternative strategies with Your PI.

Storage of potentially explosive chemicals

Follow the recommendations on the label when storing potentially explosive reagents. Store them in the explosion-proof refrigerator/freezer or in one of our explosion-proof cabinets that do not contain flammable solvents. For potentially explosive compounds (e.g., newly synthesized) with no manufacturer label, it is always best to store them in the explosion-proof refrigerator/freezer. Designated area(s) for use and storage of potentially explosive chemicals must be established. These designated areas must have a sign that at a minimum states "EXPLOSION RISK". Minimize the quantity of potentially explosive chemicals in the lab by tracking the potentially explosive compounds in the laboratory's inventory and disposing of unused compounds. Keep and store all potentially explosive chemicals away from all ignition sources such as heat, open flames, spark sources and direct sunlight

Identify unsafe reagents

Every couple of years we conduct an inventory of our chemicals. During this time note containers of any potentially explosive chemicals that do not appear safe. For example, picric acid (2,4,6-trinitrophenol) is stored safely under water but is sensitive to shock and friction if it dries out. Please refer to the SOP for peroxide forming compounds.

Ceramic or Teflon-coated spatulas

Do not transfer peroxides with metal spatulas or syringe needles; instead use a ceramic or Teflon-coated spatula for solids, or a micropipettor for liquids. Metal ions, like those in rust, can catalyze the violent decomposition of peroxides. Contact Your PI or Overman Group safety officer if you are unsure how to measure out a peroxide or other dangerous compound.

Fire-polished (ClearSeal[®]) tapered joint glassware

Compounds like diazomethane $(H_2C=N_2)$ are so unstable that sharp glass edges, or even ground glass joints, can initiate detonation. If you need to make and use diazomethane, consult with your PI and the SOP before making diazomethane for the first time. We have two types of special apparatus for preparing diazomethane as ethereal solutions—the diazomethane generator has no ground glass joints; the mini-Diazald apparatus has ClearSeal[®] fire-polished tapered joints.

Running reactions involving potentially explosive compounds (reagents, intermediates, or products)

Remember: heating or concentrating will increase the risk of explosion.

- 1. Consult with your for the first time.
- 2. Always follow a published procedure.

a. If the procedure is over 20 years old then find a recent related procedure that addresses issues of safety. Older publications may not address chemical hazards.

b. If this is your first time using or making a potentially explosive compound, then run the reaction first on a small scale.

3. Wear appropriate PPE (see above).

4. Allow for gas evolution. Use glassware with septa and attach a gas outlet of sufficient diameter to allow for the non-explosive escape of gases. Never seal explosives in a closed metal vessel.

5. Place a blast shield in front of the reaction so that you can reach around the sides to TLC your reaction.

6. Be cautious when adding potential catalysts to significant amounts of explosive reagents. Ideally, you should add potential explosives slowly (e.g., dropwise) to solutions of a catalyst – not the other way around.

7. Run reactions at the lowest temperature possible. If heat is needed, increase the temperature slowly.

8. Keep the hood sash closed while the reaction is in progress. Don't linger unnecessarily in front of the hood.

9. If the reaction involves *formation* of explosive intermediates like peroxides, quench them behind the blast shield.

10. Do not work up the reaction in a way that will concentrate potentially explosive compounds. In particular, never put solutions of potentially explosive compounds on the rotary evaporator.

11. If a solid precipitates or crystallizes and you suspect it is an explosive compound, then dissolve it in cold methanol or other appropriate solvent (the less flammable the better). Peroxides and other strong oxidizers can be reduced with aqueous bisulfite as described below. Most non-oxidizing explosive compounds are rendered safe by dilution.

Specific procedures with their own SOP

Several reactions have their own SOP, which you should consult. Some chemicals also need specific handling. Please refer to online database of MSDS before handling with such chemicals.

Synthesizing Diazomethane $(H_2C=N_2)$ - Diazomethane is a common reagent for synthesis but it should be prepared and used with caution. Light, sharp glass edges, and even swirling, have been implicated in explosions of pure diazomethane. Do not distill pure diazomethane! Consult with your PI and the SOP before for Preparing Solutions of Diazomethane for the first time.

Ozonolysis - The cleavage of C=C bonds with ozone (O_3) generates highly reactive peroxide intermediates that should not be concentrated or isolated. Consult the SOP for ozonolysis.

Disposing of potentially explosive compounds

Oxidizers: dilute, cool, reduce - Highly reactive intermediates like peroxides should be chemically reduced to make them non-explosive. Many potential explosives like peroxides, hypochlorite, and chlorate are strong oxidizers and can be reduced with bisulfite anion. If you cannot find a specific procedure for reduction of an oxidizer then do the following: 1. Dilute with chilled methanol. If necessary add other cosolvents to ensure the compound is dissolved.

2. Cool in an ice bath

3. Swirl and add saturated sodium bisulfite (NaHSO₃) dropwise, keeping the temperature low. Quenching is complete when the solution no longer tests positive with peroxide test strips.

Other explosives: dilute them - Any formulation that moves explosive molecules farther apart will reduce the potential for an explosion. The more unstable the molecule, the more dilution is required to render it safe. Nitroglycerine is shock-sensitive as a pure liquid; but when three parts nitroglycerine are mixed with one part basic Celite the resulting solid can be safely handled as sticks of dynamite. Concentrated solutions of hydrogen peroxide (90% v/v) are unsafe, yet dilute solutions of hydrogen peroxide (3% v/v) are widely sold in supermarkets.

Characterizing the dangers of potential explosives

Authors of journal articles are now directed to address the safety of their procedures. If we develop a procedure that involves isolation of a potentially explosive compound, the potential danger/safety should be characterized. Several parameters are used to assess the danger of potentially explosive compounds: friction sensitivity (e.g., ABL friction test), impact sensitivity (BAM fall hammer test) and thermal characteristics (DSC). If you believe explosive dangers of your products need to be characterized talk to your PI.

Spill and Accident Procedure

The main danger from explosive compounds is due to lacerations or trauma from an explosion. However, all compounds, including explosive compounds, are potentially toxic. If you spill any explosive compound try to dilute it or adsorb it immediately to reduce the potential for an explosion. After that, address the potential for toxic effects.

Chemical Spill Dial 911

Spill – Assess the extent of danger. Help contaminated or injured persons if safe to do so. Evacuate the spill area. Avoid breathing vapors. If possible, confine the spill to a small area using a spill kit or absorbent material. Keep others from entering contaminated area (e.g., use caution tape, barriers, etc.).

Small (<1 L) – If you have training, you may assist in the clean-up effort. Use appropriate personal protective equipment and clean-up material for chemical spilled. Double bag spill waste in clear plastic bags, label and take to the next chemical waste pick-up.

Large (>1 L) – Dial 911 and EH&S at x46200 for assistance.

Chemical Spill on Body or Clothes – Remove clothing and rinse body thoroughly in emergency shower for at least 15 minutes. Seek medical attention. *Notify supervisor and EH&S at x46200 immediately.*

Chemical Splash Into Eyes – Immediately rinse eyeball and inner surface of eyelid with water from the emergency eyewash station for 15 minutes by forcibly holding the eye open. Seek medical attention. *Notify supervisor and EH&S at x46200 immediately.*

Article VI.

Article VII. Medical Emergency Dial 911

Life Threatening Emergency, After Hours, Weekends And Holidays – Dial **911** or go to the nearest emergency room.) <u>Note</u>: All serious injuries <u>must</u> be reported to EH&S within 8 hours.

Go to the EH&S web site to file the on-line report. Follow up with a call to 949-824-6200 to report the incident.

Non-Life Threatening Emergency – Go to the UCI Student Health Center. After hours go to the nearest emergency room. <u>Note</u>: All serious injuries <u>must</u> be reported to EH&S within 8 hours. Go to the EH&S web site to file the on-line report. Follow up with a call to 949-824-6200 to report the incident.

Needle stick/puncture exposure (as applicable to chemical handling procedure) – Wash the affected area with antiseptic soap and warm water for 15 minutes. For mucous membrane exposure, flush the affected area for 15 minutes using an eyewash station. After hours go to the nearest emergency room. <u>Note</u>: All needle stick/puncture exposures <u>must</u> be reported to EH&S within 8 hours. Go to the EH&S web site to file the on-line report. Follow up with a call to 949-824-6200 to report the incident.

Decontamination/Waste Disposal Procedure

Work area: Decontamination procedures vary depending on the material being handled. Carefully inspect work areas to make sure no potentially explosive material remains. Peroxide spills can be absorbed on vermiculite and disposed of following the EH&S guidelines. Pure peroxides (in small quantities like ≤25 g) should be properly diluted before disposal. Transfer the diluted solution to a polyethylene bottle containing an aqueous solution of a reducing agent, such as ferrous sulfate or sodium bisulfite. The material can then be handled as a waste chemical; however, it must not be mixed with other chemicals for disposal. However, in case of large quantities, immediately seek assistance from EH&S UCI. All surfaces should be wiped with the appropriate cleaning agent following dispensing or handling. Waste materials generated should be treated as a hazardous waste. After each use, wipe down the immediate work area and equipment to prevent accumulation of chemical residue and thoroughly decontaminate the designated area before resuming normal laboratory work in the area.

Equipment: Decontaminate vacuum pumps or other equipment (glassware) before removing them from the designated area.

Personnel: Upon leaving the designated area, remove any personal protective equipment worn and wash hands, forearms, face, and neck. Immediately after working with highly acutely toxic materials, remove gloves and wash hands and arms with soap and water.

Schedule a hazardous waste pickup with EH&S. The container should be labeled with a waste tag that is labeled as potentially explosive.

Contaminated packaging

For spent reagent bottles containing explosive compounds rinse out the compound with enough solvent to render it safe. If you aren't sure, use 20 mL inflammable solvent for each mL or g of explosive compound.

General hazardous waste disposal guidelines:

Transfer the solutions of explosive compounds *slowly* to the hazardous waste bottle. Explosive compounds are often highly reactive and compounds in the waste container may catalyze decomposition. Adding solutions of explosive compounds to the waste will reduce the concentration, further decreasing the potential for an explosion.

Label Waste

• Hazardous waste labels must be placed on the hazardous waste container upon the start of accumulation. Labels are available online at <u>www.ehs.uci.edu/programs/enviro/</u>.

Store Waste

- Hazardous waste containers must be kept closed, except when adding waste.
- Hazardous waste containers must be stored in secondary containment to adequately contain all of the contents of the container.
- Hazardous waste containers must be inspected weekly for signs of leaks, corrosion, or deterioration.

Dispose of Waste

- Hazardous waste must be transferred to EH&S for disposal within 3 days of being generated.
- Empty Containers.
 - At no time should full or partially full containers be placed in the trash. For more information on empty container management visit www.ehs.uci.edu/programs/enviro/.
- Hazardous Waste Disposal:
 - Visit <u>www.ehs.uci.edu/programs/enviro/</u>.
 - Fill out the "Chemical Waste Collection" form.
 - EH&S will pick up your waste within 1-3 days.
- Do not dispose of chemicals by pouring them down the drain or placing them in the trash.
- Do not use fume hoods to evaporate chemicals.

Safety Data Sheet (SDS) Location

MSDSs can be found online at the UCI EH&S web site at http://www.ehs.uci.edu/msds.html

Lab-Specific Procedures

Lab-specific procedures for this class of chemicals include storing, dispensing, use in chemical reactions, use in processes (e.g., distillation, rotary evaporation, or chromatography), and disposal. Appropriate personal protective equipment and engineering controls are to be used.

General safety practices apply when working with reproductive hazards, but additional precautions are needed to set up multiple lines of defense to minimize the risks posed by these substances. These additional precautions apply to all particularly hazardous substance (adapted from <u>Prudent Practices in the Laboratory: Handling and Management of Chemical Hazards</u> :The National Academies Press: Washington, DC, 2011).

1. *PLAN carefully and think ahead.* You must have an understanding of the intrinsic hazards of the substances being used or potentially formed in any reaction. NEVER work with a reagent you are unfamiliar with without consulting your PI or an experienced co-worker *and* relevant SDS information, toxicological data, or other safety information. Always consider substituting less dangerous substances for hazardous materials and using only the smallest amount possible. For substances with unusual potential hazards, consult A Comprehensive Guide to the Hazardous Properties of Chemical Substances (Patanik, 2007) or the NIOSH website (see above). Plan for careful management of the substances through their life cycle—from acquisition and storage through safe disposal. Choose equipment and glassware that are easy to clean and decontaminate. You must also know the signs and symptoms of acute exposure, and know how to respond in an emergency.

Note: The combination of the toxic effects of two substances may be significantly greater than the toxic effect of either substance alone. Additionally, the possibility of generating toxic reaction products must also be considered during the planning phase.

- 2. **Never work alone.** It is essential that more than one person be present in the lab at all times, but especially when particularly hazarous materials are handled. Additionally, *it is your responsibility to be sure that all individuals working in the vicinity are familiar with the hazards of the experiments that you are conducting* as well as the appropriate emergency responses. Always consider the associated risk of explosions while working with potentially explosive chemicals. Potentially explosive chemicals are hazardous due to their shock senstivity and sparks. Familiarize yourself with the UCI's response and evacuation procedures. All personnel should have proper documented training in dealing with fire hazards before handling potentially explosive chemicals.
- 3. **Confine procedures involving particularly hazardous substances** that can generate dust, vapors, or aerosols to a chemical hood, glovebox, or other containment device. Procedures such as transfers to reaction vessels should be confined to a designated work area (e.g. fume hood). This area should be recognized as a place where special training/precautions/skill are required. When toxic chemicals are used in a chemical hood, the sash should be at a proper level. When working in a glove box, it should be operated under negative pressure. Use small quantities of this reagent in any given reaction (larger quantities REQUIRE the approval of PI or designee). NEVER store bulk amount of potentially explosive chemicals in common areas of lab. If the container is past its expiration, discard it immediately. If it is hard to unscrew the bottle, do not try to open it forcibly as this friction is sometimes enough to trigger the explosion. Post signs to alert others of particularly dangerous experiments.
- 4. *Wear gloves and safety glasses for protection.* Select gloves to make sure they are impervious to the chemical being used and correct thickness; consult *Prudent Practices* (link above) if you are unsure. Check gloves for integrity and appropriate composition before use. When using strong oxidants, wear fire resistant lab coats, safety glasses with side shields, and if necessary use a face shield to provide secondary protection. In some cases, respirators may be required.
- 5. *Isolate equipment*, including vacuum pumps and rotovaps, for handling of particularly hazardous chemicals.
- 6. *Practice good hygiene.* Cleanliness, order and good housekeeping practices create an intrinsically safer workplace. After using a particularly hazardous material, wash hands/neck/arms/face with soap and water. Equipment that might be contaminated (including gloves) must not be removed from the area reserved for handling toxic materials without complete decontamination. Wipe down the immediate work area and equipment to prevent accumulation of chemical residue and thoroughly decontaminate the designated area before resuming normal laboratory work in the area.

Note: Find and follow a literature experimental procedure describing the use of a reagent covered by this SOP in a related chemical transformation; if a pertinent literature protocol cannot be found, researcher MUST discuss the planned experiment with the PI (or designee) prior to use. Also no changes (such as change in temperature or pressure conditions of the reaction) in the documented literature procedure should be made without discussion and approval from PI.

Several reactions have their own SOP which you should consult. They are located in your group's Safety on Site binder.

Documentation of Training (signature of all users is required)

- Prior to conducting any work with potentially explosive compounds, designated personnel must provide training to his/her laboratory personnel specific to the hazards involved in working with this substance, work area decontamination, and emergency procedures.
- The Principal Investigator must provide his/her laboratory personnel with a copy of this SOP and a copy of the SDS provided by the manufacturer.
- The Principal Investigator must ensure that his/her laboratory personnel have attended appropriate laboratory safety training or refresher training within the last one year.

I have read and understand the content of this SOP:

Name	Signature	Date

APPENDIX:

Potentially Explosive Chemicals Used in Lab

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Appendix T: Pyrophoric Chemicals SOP

Standard Operating Procedure

Pyrophoric Chemcials

Department:	????
Date SOP written:	????
Date SOP approved by PI/lab supervisor:	????
Principal Investigator:	????
Internal Lab Safety Coordinator/Manager:	????
Lab Phone:	????
Office Phone:	????
Emergency Contact:	????
Location(s) covered by this SOP:	????

Type of SOP:
□ Pro

□ Process □ I

Hazardous Chemical

X Hazardous Class

Purpose

The purpose of this standard operating procedure is to acquaint you with safe storage, handling, and use of pyrophoric reagents.

Pyrophoric materials may ignite spontaneously on contact with atmospheric oxygen, moisture in the air, or both. Failure to follow proper handling procedures can result in fire or explosion, leading to serious injuries or death, and significant damage to facilities.

A list of the pyrophoric chemicals used in this lab is shown in the Appendix at the end of this document.

Required Training / Approvals

All work with pyrophoric chemicals requires the following prior to beginning:

- Before using a pyrophoric chemical for the first time, its use must be discussed with the Principal Investigator and all training must be well documented.
- Must be familiar with the Chemical Hygiene Plan.
- Must have documented laboratory safety training (IIPP).
- Must follow this SOP.
- Must read the relevant Safety Data Sheet (SDS, formerly referenced as Material Safety Data Sheets or MSDS).
- Must read Prudent Practices in the Laboratory: Handling and Management of Chemical Hazards - <u>http://www.nap.edu/openbook.php?record_id=4911&page=51</u>
- Any additional laboratory specific training needed to support this SOP must be referenced in the Laboratory Specific Instructions section and the signed and dated training documents must be uploaded into each assigned researchers training records. Examples include Safety Data Sheets, experimental procedures, journal articles, etc.
- Staff must have been trained and demonstrate proficiency in handling pyrophoric materials.

BEFORE working with pyrophoric reagents, users must:

- Consult with your PI and confirm that approval has been received when working with a highly hazardous material for the first time.
- Read the relevant Material Safety Data Sheets (MSDS), technical bulletins, and guidance documents to understand and how to mitigate the hazards. The MSDS must be reviewed before using an unfamiliar chemical and periodically as a reminder.
- Be familiar with this SOP and identify the safety precautions specific to the operations (<u>http://www.ehs.uci.edu/labres.html</u>)
- Consider performing a "dry run" to identify and resolve possible hazards before conducting the actual procedure.
- Users of pyrophoric materials must be trained in proper lab technique and be able to demonstrate proficiency.
- Use less toxic or hazardous substances in your experiment and minimize the amount of hazardous waste generated.
- Perform a hazard analysis and identify the failure modes in your experiment. Be prepared to handle accidents.
- Complete required EH&S safety training requirements (<u>www.ted.uci.edu</u>) and lab specific training. Address all Safety on site (SOS) issues.

It is the Principal Investigator's responsibility to ensure specific laboratory procedures and/or processes are taken into account when using this SOP. This SOP is intended to provide general guidance on how to safely work with pyrophoric agents. The reactivity of these reagents varies and should be evaluated together with the Principal Investigator/Laboratory Supervisor. If you have questions concerning the applicability of any item listed in this procedure, contact the Principal Investigator/Laboratory Supervisor of your laboratory.

Physical & Chemical Properties/Definition of Chemical Group

Pyrophoric materials ignite spontaneously in air.

Some Examples of Pyrophoric Materials

- Grignard Reagents: RMgX
- Metal alkyls and aryls: *tert*-butyllithium, *n*-butyllithium, phenyllithium
- Metal carbonyls: Lithium carbonyl, nickel tetracarbonyl
- Metal powders (finely divided): Cobalt, iron, zinc, zirconium, lithium
- Metal hydrides: Sodium hydride, potassium hydride, diisobutylaluminum hydride
- Nonmetal hydrides: Diethylarsine, diethylphosphine
- Non-metal alkyls: R₃B, R₃P, R₃As
- Phosphorus: white phosphorous
- Potassium
- Sodium
- Gases: Silane, dichlorosilane, diborane, phosphine, arsine

A more extensive list of pyrophoric compounds can be found in Bretherick's *Handbook of Reactive Chemical Hazards*

Potential Hazards/Toxicity

Physical Hazards

- Researchers working with pyrophoric materials must be proficient and **must not work** alone!
- Many pyrophorics are sold as solutions in flammable solvents, which may exacerbate any dangerous reactions that can occur with misuse of these reagents.
- Be especially vigilant when working with *tert*-butyllithium (*t*-BuLi) which is **extremely pyrophoric**.
- Pyrophorics tend to be toxic with common hazards being damage to the liver, kidneys, and central nervous system as well as tetratogenicity.
- Other common hazards include corrosivity, water reactivity, peroxide formation (see SOP for peroxide forming reagents).
- Pyrophorics can lead to explosions on contact with air and/or water. See SOPs for potentially explosive compounds for more information.

Health Hazards

Some compounds under this category are toxic and may be dissolved in a flammable solvent. Other common hazards include corrosivity and peroxide formation. May cause damage to liver, kidney, and mucus membranes, and central nervous system.

Personal Protective Equipment (PPE)

Ensure that all lab personnel have completed and reviewed the PPE assessment tool.

Eye Protection

- Chemical splash goggles or safety glasses that meet the ANSI Z.87.1 1989 standard must be worn whenever handling pyrophoric chemicals. Ordinary prescription eyeglasses will NOT provide adequate protection. When there is the potential for splashes, goggles must be worn, and when appropriate, a face shield for added protection.
- A face shield, worn over safety eyewear, is required any time there is a risk of explosion, large splash hazard, or a highly exothermic reaction. All manipulations of pyrophoric chemicals that pose this risk should be carried out in a fume hood with the sash in the lowest feasible position.

Skin Protection

- Gloves must be worn when handling pyrophoric chemicals. Be sure to use adequate protection to prevent skin exposures. Sigma-Aldrich recommends the use of nitrile gloves underneath neoprene gloves. Flame retardant gloves should be used for handling large quantities of these chemicals.
- A lab coat made from fire retardant material is recommended for labs using these reagents routinely. Lab coats need to be buttoned and fit properly to cover as much skin as possible.
- Appropriate shoes that cover the entire foot (closed toe, closed heel, no holes in the top) and long pants must be worn.
- Avoid wearing clothing made out of highly flammable synthetic fabrics such as acrylic or polyester.

Engineering Controls

Have the proper equipment and the emergency phone number (9-1-1) readily available for any emergencies. The recommended fire extinguisher is a standard dry powder (ABC) type. DO NOT use a carbon dioxide fire extinguisher or water to attempt to extinguish a pyrophoric material fire as these types of extinguishers can actually enhance the combustion of some pyrophoric materials. A small beaker of dry sand or soda ash (lime) in the work area is useful to extinguish any small fire that occurs at the syringe tip and to receive any last drops of reagent from the syringe.

Eyewash/ Safety Shower

• A combination eyewash/safety shower should be within 10 seconds travel time from any location where pyrophoric chemicals are used. Inside the laboratory is optimum. Bottle type eyewash stations are not acceptable.

- Verify that your fume hood has been checked in the last 12 months.
- Many pyrophoric chemicals release noxious or flammable gases, and some pyrophoric materials are stored under kerosene or mineral oil. These materials must be handled in a laboratory hood with sash in the lowest feasible position

Safety shielding

• Safety shielding is required any time there is a risk of explosion, splash hazard or a highly exothermic reaction. Portable shields may be used to provide additional protection.

Glove (dry) box

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

Inert atmosphere manifold (Schlenk Line)

 Nitrogen or argon lines are extremely useful when performing manipulations of air- and/or water-sensitive reagents. If a glove box cannot be used, proper use of an inert atmosphere manifold can help minimize exposure of these reagents to air and water.

Gas Cabinets

- Storage of pyrophoric gases is described in the California Fire Code, Chapter 41. Gas cabinets, with appropriate remote sensors and fire suppression equipment, are required.
- Gas flow, purge and exhaust systems should have redundant controls to prevent pyrophoric gas from igniting or exploding. All pyrophoric gases must have Restricted Flow Orifices (RFO) installed on the cylinder. Contact your gas supplier for assistance.
- Emergency back-up power should be provided for all electrical controls, alarms and safeguards associated with the pyrophoric gas storage and process systems.

First Aid Procedures

Before beginning to work with pyrophoric chemicals, review the relevant Material Safety Data Sheet (MSDS) and appropriate chemical safety resources as listed in the Training/Approval section of this document. Develop specific procedures for emergency response and chemical exposure or injury to staff, including any special first aid measures required for the relevant chemical.

Additional special instructions for Department of Chemistry/Biochemistry personnel only:

- Report serious incidents immediately: Call 9-1-1
- Immediately secure any incident scene from all access and preserve all evidence for no less than 24 hours.

Chemicals may enter the body through four routes: inhalation, ingestion, injection, or contact with the skin and eyes. With each route of exposure, the likelihood of injury depends on the toxicity of the chemical involved, the concentration of the material, and the duration of contact. For all exposures:

• Seek immediate medical attention.

- Call Campus Police at 911 and request an ambulance if transportation is necessary.
- Call the Poison Control System, (800) 222-1222, if additional information is needed.
- If you're injured, experience a hazardous material exposure, or develop a job-related illness as a result of chemical exposure, seek medical treatment immediately.

Special Handling and Storage Requirements

Pyrophoric reagents can be handled and stored safely provided exposure to atmospheric oxygen and moisture is avoided.

Some pyrophoric materials cannot be stored in unsprinklered buildings; check list of restricted chemicals at:

http://www.ehs.uci.edu/programs/fire/ChemicalsNotPermittedInUnsprinkleredBuildings.pdf

- Use and store minimal amounts of pyrophoric chemicals.
- Do not store pyrophoric chemicals with flammable materials or in a flammable liquids storage cabinet. Containers carrying pyrophoric materials must be clearly labeled with the correct chemical name, in English, and hazard warning.
- Store as recommended in the MSDS. A nitrogen-filled desiccator or glove box is a suitable storage location.

• If pyrophoric reagents are received in a specially designed shipping, storage or dispensing container, (such as the Aldrich Sure/Seal packaging system) ensure that the integrity of that container is maintained.

• Ensure that sufficient protective solvent, oil, kerosene, or inert gas remains in the container while the material is stored.

• NEVER return excess chemical to the original container. Small amounts of impurities introduced into the container may cause a fire or explosion.

- For storage of excess chemical, prepare a storage vessel in the following manner:
 - Dry a new empty containers thoroughly
 - Select a septum that fits snugly into the neck of the vessel

• Insert septum into neck in a way that prevents atmosphere from entering the clean, dry (or reagent filled) flask.

• Insert a needle to inject inert gas and to maintain a blanket of dry, inert gas above the reactive reagent and quickly insert a second needle to vent the flask.

• Once the vessel is fully purged with inert gas, remove the vent needle and add the reagent carefully, then remove the gas line.

• For long-term storage, the septum should be secured with a copper wire.

Working with pyrophoric reagents

Never work alone. At least one other person must be present in the same laboratory and must be informed when any work involving pyrophoric reagents are carried out.

Finely divided pyrophoric solids must be transferred under an inert atmosphere in a glove box. Liquids may be safely transferred employing proper syringe, cannulation, or Schlenk techniques and equipment as discussed in the Aldrich Technical Information Bulletin AL-134 (<u>http://www.sigmaaldrich.com/content/dam/sigma-</u> <u>aldrich/docs/Aldrich/Bulletin/al_techbull_al134.pdf</u>).

Pyrophoric gases should be handled in compliance with the California Fire Code, Chapter 41.

- Eliminate or substitute for a less hazardous material when possible.
- Design your experiment to use the least amount of material possible to achieve the desired result.
- Minimize the quantity of pyrophoric reagents used and stored and use the smallest quantity of material practical.
- Verify your experimental set-up and procedure prior to use.
- Inform colleagues that this material will be used and where.
- Only use if the area is properly equipped with a certified eye wash/safety shower within ten seconds of travel.
- If possible, run reactions involving pyrophoric reagents in an inert atmosphere glove box.
- If a glove box cannot be used, it is better to do multiple transfers of small volumes than to attempt to handle larger quantities. Consider using the cannulation method when transferring more than 20 mL.
- Make sure the area where the experiment is being preformed has been adequately prepared for the experiment.
- Designate a fume hood or glove box for hazardous work.
- Keep combustible materials, including paper towels and Kimwipes, away from pyrophoric reagents.
- Remove all excess and nonessential chemicals and equipment from the fume hood or glove box where pyrophoric reagents are in use.

Spill and Accident Precautions

- A container of powdered lime or dry sand should be kept within arm's length when working with a pyrophoric material, which may be adequate to smother a small spill that might occur.
- **DO NOT** use water on a pyrophoric reagent fire, as it can make the incident even worse.
- Do not use combustible materials like paper towels to clean up a spill, as these may increase the risk of ignition with a pyrophoric reagent. Soda ash (powdered lime) or dry sand may cover and contain any small spill that occurs.
- The recommended fire extinguisher is a standard dry powder (ABC) type and should be within immediate reach in the event of an incident.
- Class D extinguishers are recommended for combustible solid metal fires (e.g, sodium, LAH), but not for organolithium reagents.

Chemical Spill

Spill – Assess the extent of danger. Help contaminated or injured persons if safe to do so. Evacuate the spill area. Avoid breathing vapors. If possible, confine the spill to a small area using a spill kit or absorbent material. Keep others from entering contaminated area (e.g., use caution tape, barriers, etc.).

Small (<100 g) – Even small spills of a pyrophoric material, especially liquids, can be extremely hazardous, especially if other flammable compounds or solvents are in the lab or fume hood. If the fire can be readily contained and you have had training, you may assist in the clean-up effort. Use appropriate personal protective equipment and clean-up materials for chemical spilled. Double bag neutralized waste in clear plastic bags or approved container(s), label and take to the next chemical waste pick-up.

Large (>100 g) – Dial 911 and EH&S at x46200 for assistance.

Chemical Spill on Body or Clothes – Remove contaminated clothing and rinse body thoroughly in emergency shower for at least 15 minutes. Seek medical attention. Notify supervisor and EH&S at x46200 immediately.

Chemical Splash Into Eyes – Immediately rinse eyes and inner surface of eyelids with water from the emergency eyewash station for at least 15 minutes by forcibly holding the eye open. **Seek immediate medical attention. Notify supervisor and EH&S at x46200 immediately.**

Article VIII. Medical Emergency

a. Life Threatening Emergency – Dial 911 if the condition is LIFE THREATENING or REQUIRES IMMEDIATE MEDICAL ATTENTION

b. Non-Life Threatening Emergency – Notify your supervisor or faculty staff if condition is not life threatening.

c. Needle Stick/puncture Exposure (as applicable to chemical handling procedure) – Wash the affected area with antiseptic soap and warm water for 15 minutes. For mucous membrane exposure, flush the affected area for 15 minutes using an eyewash station.

All serious injuries <u>must</u> be reported to EH&S at **x46200** within 8 hours.

ALL WORK RELATED INJURIES MUST BE REPORTED via the On-line Incident Form <u>https://www.ehs.uci.edu/apps/hr/index.jsp</u> or call Human Resources, Workers Compensation (949) 824-9152.

Decontamination/Waste Disposal Procedure

Disposal of Pyrophoric Reagents

- A container with any residue of pyrophoric materials should never be left open to the atmosphere.
- Unused or unwanted pyrophoric materials must be destroyed by transferring the materials to an appropriate reaction flask under inert atmosphere for hydrolysis and/or neutralization with adequate cooling.
- To the flask should be added an inert dry solvent, such as toluene or THF, to dilute the reactive reagent under an atmosphere of dry nitrogen or argon.
- The stirred solution should be neutralized by the drop-wise addition of a ice-chilled protic solvent, such as isopropyl alcohol. **Never** add water or a protic solvent **directly to** a pyrophoric reagent.
- Before disposal, the flow of inert gas should be stopped to expose the quenched solution to the ambient atmosphere for a 24-hour period at which time standard waste disposal practices can be followed.
- Once emptied, the flask should then be triple rinsed with isopropyl alcohol and left to dry in the back of a fume hood.
- The original container should be triple-rinsed with a dry inert solvent under a flow of inert gas. These rinses should be then treated as described above. The triple-rinsed container should be left open in back of a hood exposed to the ambient atmosphere for at least a

week to ensure all remaining residue has been quenched. After a week, the container should then be triple rinsed again with isopropyl alcohol.

Disposal of Pyrophoric Contaminated Materials

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

General hazardous waste disposal guidelines

Label Waste

• Hazardous waste labels must be placed on the hazardous waste container upon the start of accumulation. Labels are available online at www.ehs.uci.edu/programs/enviro/.

Store Waste

- Hazardous waste containers must be kept closed, except when adding waste.
- Hazardous waste containers must be stored in secondary containment to adequately contain all of the contents of the container.
- Hazardous waste containers must be inspected weekly for signs of leaks, corrosion, or deterioration.

Dispose of Waste

- Hazardous waste must be transferred to EH&S for disposal within 6 months of being generated.
- Empty Containers: At no time should full or partially full containers be placed in the trash. For more information on empty container management visit <u>http://www.ehs.uci.edu/programs/enviro/</u>
- Hazardous Waste Disposal: visit www.ehs.uci.edu/programs/enviro/.
- Fill out the "Chemical Waste Collection" form.
- EH&S will pick up your waste within 1-3 days.
- Do not dispose of chemicals by pouring them down the drain or placing them in the trash.
- Do not use fume hoods to evaporate chemicals.

Safety Data Sheet (SDS) Location

Online SDS can be accessed at <u>http://www.ehs.uci.edu/msds.html</u>.

Lab-Specific Procedures

Lab-specific procedures for this class of chemicals include storing, dispensing, use in chemical reactions, use in processes (e.g., distillation, rotary evaporation, or chromatography), and disposal. Appropriate personal protective equipment and engineering controls are to be used.

Lithium Aluminum Hydride Reactions

"Warning on the use of aluminum lithium hydride (LAH): Following the investigation of a laboratory explosion, Dr. M. L H. Green of the University of Oxford has warned that the following precautions are essential for the safe use of lithium aluminum hydride (LAH). The measures are to prevent overheating of the hydride and dissociation to finely divided aluminum, which can then undergo thermite-type reactions with compounds (or solvents) containing combined oxygen or halogen.

- All apparatus and reactants should be perfectly dry, and reaction should be run rigorously under nitrogen, with the reaction temperature below 60 °C at all times.
- Order of addition is important. Always first add the hydride to the solvent in the nitrogenpurged apparatus, before the addition of other reactants.
- The hydride should never be allowed to form a crust above the level of the liquid or to settle to the bottom, so efficient and gentle stirring is absolutely essential.
- To prevent local overheating of the reaction vessel, heating mantles should never be used; always used an oil bath as heat source.
- After reduction has been effected, destroy excess LAH by slow and careful addition of dry ethyl acetate (preferably diluted with inert solvent), again under nitrogen and keeping the temperature below 60 °C. All LAH reactions should be carried out behind suitable protective screens."
- May ignite when ground in mortar.
- Use in dehydrating bis(2-methyoxyethyl)ether has resulted in explosions; other experiments involving boron trifluoride diethyl etherate, dibenzoyl peroxide, 1,2-dimethyoxyethane, ethyl acetate, and fluoroamides also resulted in explosions. Vigorous reactions with pyridine and tetrahydrofuran have also been reported.

Organolithium Reagents

Organolithium reagents are pyrophoric upon exposure to air or water. They must be handled under an inert atmosphere to prevent exposure to air and/or water. Most organolithium reagents are purchased in a flammable organic solvent. Be especially cautious when working with *tert*-butyllithium, which is extremely pyrophoric.

- All apparatus and reactants should be perfectly dry, and reactions should be run rigorously under an inert gas with an oil bubbler to release pressure. If lithium metal is a reactant, argon must be used as the inert gas instead of nitrogen. Nitrogen reacts exothermically with lithium metal to form lithium nitride (Li₃N).
- When using an organolithium reagent, keep combustible materials, including paper towels and Kimwipes, away from the reagent.
- The syringe used to transfer the organolithium reagent should never be more than ¾ full, and multiple transfers of the reagent in small volumes are better than one large volume. If transferring large volumes of more than 20 mL, transferring the reagent via the cannula method is recommended.
- If working with volumes greater than 1 L a face shield should be employed to provide additional eye protection.
- Reactions with pyrophoric chemicals should never be run while alone in the lab.
- Immediately after use, the needle and syringe should be quenched by dilution with heptane, followed by addition to an isopropyl alcohol and ice bath.
- Standard dry powder (ABC) type or dry sand are recommended to put out a small fire, never use a carbon dioxide, water, or halogenated hydrocarbon fire extinguisher to

extinguish pyrophoric materials, as these will exacerbate the fire. Class D fire extinguishers are not recommended for organolithium reagents.

Other Organometallic Chemicals (eg. Organozinc and Organoaluminum)

Other organometallic chemicals should be handled in the same way as organolithium reagents. Standard dry powder (ABC) type, or Class D fire extinguishers are recommended. Dry sand and sodium carbonate are also recommended to smother and cover small spills.

Reactions of Other Pyrophoric Water Reactive Chemicals

Alkali and alkaline earth metals (such as sodium, potassium, lithium, magnesium, calcium, powdered aluminum) should be stored and handled so they cannot contact carbon dioxide, carbon tetrachloride and other chlorinated hydrocarbons, water, and water- or CO₂-containing fire extinguishers.

Besides water, other reagents may be incompatible with water-reactive compounds. Below is a small list of incompatibles for certain reagents (excerpted from "Hazards in the Chemical Laboratory, 4th Edition," Edited by L. Bretherick. London, The Royal Society of Chemistry, 1986).

Aluminum hydride: May explode spontaneously at ambient temperatures; violent decomposition in certain methyl ethers in presence of carbon dioxide; forms explosive complexes with tetrazoles.

Aluminum metal (particularly, finely powdered aluminum): Violent or explosive reaction with numerous oxidants, butanol, halocarbons, halogens, HCl, mercury salts, silver chloride.

Calcium: Pyrophoric when finely divided. Reacts explosively with PbCl₂, P₂O₂, S, N₂O₄.

Calcium carbide: Vigorous reaction with boiling methanol; forms highly sensitive explosives with silver nitrate solutions; explosive with sodium peroxide solutions.

Cerium: Reaction with zinc is explosively violent.

Diethylzinc: Pyrophoric in air; reacts violently with water, violent reaction with diiodomethane/alkene mixtures, methanol, halogens, AsCl₃, PCl₃, SO₂, nitro compounds.

Dimethylzinc: Ignites in air and explodes in oxygen.

Lithium: Finely divided metal may ignite in air; will burn in nitrogen or carbon dioxide and is difficult to extinguish once alight; reacts violently with BrF₅ and explosively with diazomethane; mixtures with halocarbons will explode on impact; ignites on contact with nitric acid or sulfur. Powdered Li may explode with bromobenzene.

Lithium hydride: ignites in warm air; mixtures with liquid oxygen are detonable explosives.

Magnesium: As a fine powder dispersed in air, it is a serious explosion hazard; reaction with beryllium fluoride is violent; powdered metal may react or explode with contact with chloromethane, chloroform, carbon tetrachloride. Ignites if finely divided on heating in iodine vapor; reacts vigorously with certain cyanides, metal oxides, metal oxo-salts, methanol. Mixtures with methanol and water are detonatable.

Phosphorus pentasulfide: P_4S_{10} ignites by friction, sparks or flames; it heats and may ignite with limited amounts of water.

Potassium: Explosions have occurred when old, heavily-crusted potassium metal has been cut with a knife. Such old stocks should be disposed of uncut. Reacts readily with CO to form

explosive carbonyl; K does not react with air or oxygen in complete absence of moisture, but in its presence oxidation becomes fast, and melting and ignition takes place; prolonged but restricted access to air results in the formation of coatings of yellow superoxides on top of the monoxide—percussion or dry cutting of the metal brings traces of residual oil into contact with the superoxide and a very violent explosion occurs. Reacts to form shock sensitive compounds with contact with halocarbons; ignites in fluorine and chlorine; explodes or reacts violently with bromine, HI, mercury, metal halides and oxides, non-metal halides and oxides, oxidants, sulfuric acid.

Sodium: Dispersions of sodium in volatile solvents become pyrophoric when solvent evaporates; can react dangerously with chloroform/methanol, diazomethane, DMF, fluorinated compounds, halocarbons, halogens, mercury, metal halides and oxides, non-metal halides as oxides, oxidants, bromobenzene, SnO₂, POCl₃, sulfides. Mixtures with SO₂F₂, SiCl₄, CS₂, alkyl oxalates, or aromatic nitro compounds are shock sensitive.

Sodium hydride: Reacts vigorously with acetylene, DMSO, sulfur, SO₂; exotherms with DMF at 40 °C; dry powder ignites in air.

Zinc: Forms pyrophoric compounds with halocarbons. Reacts violently with MnCl₂, KO₂, TiO₂, ZnO₂, sulfur, potassium chlorate, and ammonium nitrate.

Used Hydrogenation Catalysts

When setting up a hydrogenation reaction, the solid catalyst should be added first and the vessel flushed with an inert gas, followed by the solvent. An inert gas should first be introduced into the reaction vessel before filling the vessel with hydrogen gas. Hydrogenation reactions run under pressure should be covered by a blast shield for additional protection. If filtering the reaction mixture through Celite (or similar filter aid), care should be taken to not let the filter cake dry out which could cause ignition of the catalyst.

Metal Carbonyls

Metal carbonyls should be handled under an inert environment in a fume hood. A flame resistant lab coat, chemical splash goggles or safety glasses, and gloves should be worn when working with metal carbonyls. PVC gloves are recommended in most cases; however check the glove charts to determine the recommended glove type for a particular metal carbonyl. These reagents are potentially explosive if heated to 60 °C. If swallowed, drink 1-2 glasses of water and induce vomiting if the person is conscious.

NOTE

Any deviation from this SOP requires approval from PI.

Documentation of Training (signature of all users is required)

- Prior to conducting any work with pyrophoric reagents, designated personnel must provide training to his/her laboratory personnel specific to the hazards involved in working with this substance, work area decontamination, and emergency procedures.
- The Principal Investigator must provide his/her laboratory personnel with a copy of this SOP and a copy of the SDS provided by the manufacturer.
- The Principal Investigator must ensure that his/her laboratory personnel have attended appropriate laboratory safety training or refresher training within the last one year.

I have read and understand the content of this SOP:

Name	Signature	Date

APPENDIX: Pyrophoric Chemicals Used in Lab

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Appendix U: Regulated Carcinogens SOP

Standard Operating Procedure

Regulated Carcinogens

Department:	????
Date SOP written:	????
Date SOP approved by PI/lab supervisor:	????
Principal Investigator:	????
Internal Lab Safety Coordinator/Manager:	????
Lab Phone:	????
Office Phone:	????
Emergency Contact:	????
Location(s) covered by this SOP:	????

Type of SOP:
□ Process
☑ Hazardous ChemicalX Hazardous Class

Purpose

The purpose of this standard operating procedure is to acquaint you with potentially carcinogenic chemicals, how to handle carcinogenic materials, and safety practices. Above all, use a combination of common sense and chemical sense.

A list of the regulated carcinogens used in this lab is shown in the Appendix at the end of this document.

Definition of Chemical Group

According to *Prudent Practices in the Laboratory: Handling and Management of Chemical Hazards* (section 4.C.3.6 Carcinogens) The National Academies Press: Washington, DC, 2011.

"A carcinogen is a substance capable of causing cancer."

Compounds are considered carcinogenic if they are:

1. regulated by Cal/OSHA as a carcinogen.

2. listed "known to be carcinogens" by the National Toxicology Program (NTP)

3. listed under Group 1 ("carcinogenic to humans") by the International Agency for Research on Cancer (IARC)

4. listed in either Group 2A or 2B by IARC or under the category, "reasonably anticipated to be carcinogens" by NTP, and causes statistically significant tumor incidence in experimental animals in accordance with any of the following criteria:

Carcinogenic Exposure can be considered:

(a) 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;

(b) After repeated skin application of less than 300 mg/kg of body weight per week; or

(c) After oral dosages of less than 50 mg/kg of body weight per day.

Table: Regulated carcinogen

<u>13 '</u>	Listed" Cal/OSHA Carcinogens	Other Regulated Carcinogens (not a complete
	2-acetylaminofluorene	<u>list)</u>
	4-aminodiphenyl	
	benzidine and its salts	
	3,3'-dichlorobenzidine and its salts	□ benzene
		butadiene
	4-dimethylaminoazobenzene	🗌 cadmium
	alpha-naphthylamine	carbon tetrachloride
	beta-naphthylamine	formaldehyde
	4-nitrobiphenyl	<pre>ethylene dibromide</pre>
	N-nitrosodimethylamine	<pre>ethylene oxide</pre>
	beta-propiolactone	methylene chloride (dichloromethane)
	bis-chloromethyl ether	
	methyl chloromethyl ether	
	ethyleneimine	vinyl chloride.
		Other:

A list of chemicals known to the State of California to cause cancer can be found at http://www.oehha.ca.gov/prop65/prop65 list/files/filesp65single110112.pdf

Handling of Carcinogenic Chemicals

Here are general guidelines on how to handle carcinogenic chemicals. Refer to specific compounds' SOPs and SDS for specific procedures.

1. a) Work in a ventilated hood or glove box when opening carcinogenic chemical containers to control the movement of chemical vapors.

b) Work in a ventilated area when weighing out chemicals.

- 2. Use the minimum amount of carcinogenic chemicals necessary for experiments.
- 3. Dispose of carcinogenic chemicals in the proper/designated waste containers.
- 4. Wear the proper PPE (as mentioned below) that protects one as well as allows one to work efficiently.
- 5. Use of a regulated carcinogen on a scale larger than 10 mmol requires the approval of the PI.

Think ahead: Before you work with potentially carcinogenic chemicals review the relevant Material Safety Data Sheet and appropriate chemical safety resources. Review specific procedures for emergency response, chemical exposure, or injury to staff, including any special first aid measures. Above all, anticipate accidents before they occur and <u>use common sense</u>! Wear protective eyewear and work with the hood sash closed.

Potential Hazards/Toxicity

The development of tumors are some of the main hazards associated with the chemicals under this category. Chemicals in this category may exhibit reproductive effects, other long term health effects, and acute health effects, which will vary based on the individual compound.

Hazard Identification Resources include:

Safety Data Sheet resources at<u>http://www.ehs.uci.edu/msds.html</u> Risk Assessment Tool at<u>http://www.ehs.uci.edu/programs/labres/LABRAT.pdf</u> High Hazard Chemicals/Process Screening Tool at <u>High Hazard</u> <u>Chemicals/Processes Screening Tool</u>

Personal Protective Equipment (PPE)

Respiratory protection is generally not required for lab research, provided the appropriate engineering controls are employed. Respirators should be used only under any of the following circumstances:

• As a last line of defense (i.e., after engineering and administrative controls have been exhausted).

• When Permissible Exposure Limit (PEL) has exceeded or when there is a possibility that PEL will be exceeded.

- Regulations require the use of a respirator.
- Chemical Hygiene Plan

• An employer requires the use of a respirator.

• There is potential for harmful exposure due to an atmospheric contaminant (in the absence of PEL)

• As PPE in the event of a chemical spill clean-up process

Lab personnel intending to use/wear a respirator mask must be trained and fit-tested by EH&S. This is a regulatory requirement. If you think that your process may require respirator use, contact EH&S for assistance (<u>http://www.ehs.uci.edu/programs/ih/respiratory.html</u>)

Hand Protection

Appropriate disposable nitrile gloves should be worn when dealing with small quantities of carcinogenic chemicals. Lab workers should consult EH&S for appropriate selection of gloves when dealing with chemicals for a prolonged period of time. Certain carcinogens should be handled only inside the glove box. Some of the carcinogenic chemicals can pose reproductive hazards as well *(please also refer to SOP for reproductive hazards)*, so appropriate selection of gloves should be done.

NOTE: Consult with your preferred glove manufacturer to ensure that the gloves you plan on using are compatible with the carcinogen you are using.

Refer to glove selection chart from the links below: <u>http://www.ansellpro.com/download/Ansell_8thEditionChemicalResistanceGuide.pdf</u> <u>OR</u> <u>http://www.allsafetyproducts.biz/page/74172</u> OR <u>http://www.showabestglove.com/site/default.aspx</u> OR http://www.mapaglove.com/

Eye Protection

ANSI approved properly fitting safety glasses with side shields should be worn. When potential of a splash exists other eye protection or face shield protection should be worn. Faceshields are designed to protect the face, not the eye, and should only be used WITH safety glasses or goggles, never alone.

Skin and Body Protection

Appropriate street clothing (long pants, long sleeves, close-toed shoes) along with proper lab coats should be worn at all times while handling these chemicals.

Hygiene Measures

Wash your hands thoroughly and immediately after handling. Remove contaminated clothing and wash before reuse. Avoid breathing vapors, mist or gas.

If you have questions concerning the applicability of any item listed in this procedure consult the PI.

Engineering Controls

Fume Hood

Reactions involving potentially carcinogenic reagents, intermediates, or products should be conducted in a clean, working chemical hood with the sash lowered. Ensure that adequate

space is available in the hood to perform the work. A glove box can also be used for handling these chemicals. As much as possible, it is preferable to keep reagents and reaction vessels towards the back of the fume hood. All areas where the chemicals are stored or manipulated should be labeled with appropriate signs.

Required Training / Approvals

All work with regulated carcinogens requires the following prior to beginning work:

1. All work with regulated carcinogens must be pre-approved by the Principal Investigator and all training must be well documented.

- 2. Must be familiar with the Chemical Hygiene Plan.
- 3. Must have documented Laboratory Safety Principles/IIPP training.
- 4. Must follow this SOP.

5. Must read the relevant Safety Data Sheet (formerly referenced as Material Safety Data Sheets).

 Must read Prudent Practices in the Laboratory: Handling and Management of Chemical Hazards (section 4.C.3.6. Carcinogens and 6.D. Working with Substances of High Toxicity).
 Any additional laboratory specific training required to support this SOP must be referenced in the Laboratory Specific Instructions section and the signed and dated training documents must be uploaded into each assigned researcher's training records. Examples include Safety Data Sheets, experimental procedures, journal articles, etc.

Administrative Controls

1. <u>Never</u> work alone. At least one other person must be present in the same laboratory when any work involving carcinogens is conducted.

2. Eliminate or substitute for a less hazardous material when possible.

3. Design your experiment to use the least amount of material possible to achieve the desired result.

4. Verify your experimental set-up and procedure prior to use.

5. Inform colleagues this material will be used and where.

6. Only use if the area is properly equipped with a certified eye wash and safety shower within ten seconds of availability.

7. Consult with the PI if work involves large quantities.

First Aid Procedures

Consult the SDS for the compound being used. General first aid procedures for hazardous chemicals typically include:

If inhaled

Move person into fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Seek medical aid immediately.

In case of skin contact

Wash skin with soap and water for at least 15 minutes while removing contaminated clothing and shoes. Wash clothing before reuse. Thoroughly clean shoes before reuse. Consult a physician.

In case of eye contact

Flush eyes with plenty of water for at least 15 minutes. Consult a physician.

If swallowed

Do NOT induce vomiting unless directed by medical personnel. Never give anything by mouth to an unconscious person. Seek medical attention immediately.

Special Handling and Storage Requirements

GENERAL RULE: WORK WITH LESS

Reduce the quantity of potentially carcinogenic compounds that you work with. Buy less; store less; use less.

Storage of potentially carcinogenic chemicals

It is essential that hazardous chemicals be stored separately from all chemicals with which they may react. Keep in tightly sealed containers, away from heat and sources of ignition. Ensure secondary containment and segregation of incompatible chemicals per guidance within the Chemical Hygiene Plan. Also, follow any substance specific storage guidance provided in Safety Data Sheet (SDS).

Follow the recommendations on the label when storing potentially carcinogenic reagents. Store them in an appropriate chemical refrigerator/freezer within the lab or in one of our explosion-proof cabinets that do not contain flammable solvents (depending on the chemical storage information). For potentially carcinogenic compounds (e.g., newly synthesized) with no manufacturer label, it is always best to store them in an appropriate chemical refrigerator/freezer within the lab.

Identify unsafe reagents

During periodic inventory note containers of any potentially carcinogenic chemicals that do not appear safe and contact EHS at x46200 for assistance with disposal.

Specific carcinogens with their own SOP

Several carcinogens have their own SOP which you should consult. They are located in Appendix C of this docuement.

Spill and Accident Procedure

Chemical Spill Dial 911

Spill – Assess the extent of danger. Help contaminated or injured persons. Evacuate the spill area. Avoid breathing vapors. If possible, confine the spill to a small area using a spill kit or absorbent material. Keep others from entering contaminated area (e.g., use caution tape, barriers, etc.).

Small (<1 L) – If you have training, you may assist in the clean-up effort. Use appropriate personal protective equipment and clean-up material for chemical spilled. Double bag spill waste in clear plastic bags, label and take to the next chemical waste pick-up.

Large (>1 L) – Dial 911 and EH&S at x46200 for assistance.

Chemical Spill on Body or Clothes – Remove clothing and rinse body thoroughly in emergency shower for at least 15 minutes. Seek medical attention. *Notify supervisor and EH&S at x46200 immediately.*

Chemical Splash Into Eyes – Immediately rinse eyeball and inner surface of eyelid with water from the emergency eyewash station for 15 minutes by forcibly holding the eye open. Seek medical attention. *Notify supervisor and EH&S at x46200 immediately.*

Article IX.

Article X. Medical Emergency Dial 911

Life Threatening Emergency, Business Hours, After Hours, Weekends And Holidays –Dial **911** CALL 911 if the condition is LIFE THREATENING or REQUIRES IMMEDIATE MEDICAL ATTENTION.. <u>Note</u>: All serious injuries <u>must</u> be reported to EH&S at **x46200** within 8 hours. Complete online incident report at <u>https://www.ehs.uci.edu/apps/hr/index.jsp</u>

Non-Life Threatening Emergency – Notify your supervisor or faculty staff if condition is not life threatening.

Needle stick/puncture exposure (as applicable to chemical handling procedure) – Wash the affected area with antiseptic soap and warm water for 15 minutes. For mucous membrane exposure, flush the affected area for 15 minutes using an eyewash station. ALL WORK **RELATED INJURIES MUST BE REPORTED via the On-line Incident Form** <u>https://www.ehs.uci.edu/apps/hr/index.jsp</u> or call Human Resources, Workers **Compensation (949) 824-9152.**

Decontamination/Waste Disposal Procedure

General hazardous waste disposal guidelines:

Transfer the solutions of carcinogenic compounds *slowly* to the hazardous waste bottle. Compounds can often be highly reactive and compounds in the waste container may catalyze decomposition.

Label Waste

• Hazardous waste labels must be placed on the hazardous waste container upon the start of accumulation. Labels are available online at <u>www.ehs.uci.edu/programs/enviro/.</u>

Store Waste

- Hazardous waste containers must be kept closed, except when adding waste.
- Hazardous waste containers must be stored in secondary containment to adequately contain all of the contents of the container.
- Hazardous waste containers must be inspected weekly for signs of leaks, corrosion, or deterioration.
- Store hazardous waste in closed containers, in secondary containment and in a designated location. Carcinogenic compounds may generate gases as they decompose; leave the lid loose enough to allow gases to escape. When the container is ready for pick up, seal the lid tight – at that point gas evolution should be largely complete.
- Double-bag dry waste using transparent bags
- Waste must be under the control of the person generating & disposing of it

Dispose of Waste

 Hazardous waste must be transferred to EH&S for disposal within 6 months of being generated.

- Empty Containers: At no time should full or partially full containers be placed in the trash. For more information on empty container management visit www.ehs.uci.edu/programs/enviro/.
- Hazardous Waste Disposal:
 - Visit <u>www.ehs.uci.edu/programs/enviro/</u>.
 - Fill out the "Chemical Waste Collection" form.
 - EH&S will pick up your waste within 1-3 days.
- Do not dispose of chemicals by pouring them down the drain or placing them in the trash.
- Do not use fume hoods to evaporate chemicals.

Safety Data Sheet (SDS) Location

MSDSs can be found online at accessed at http://www.ehs.uci.edu/msds.html..

Designated Area

Experiments involving carcinogens should be confined to a fume hood.

Lab-Specific Procedures

Lab-specific procedures for this class of chemicals include storing, dispensing, use in chemical reactions, use in processes (e.g., distillation, rotary evaporation, or chromatography), and disposal. Appropriate personal protective equipment and engineering controls are to be used.

General safety practices apply when working with carcinogens, but additional precautions are needed to set up multiple lines of defense to minimize the risks posed by these substances. These additional precautions apply to all particularly hazardous substance (adapted from <u>Prudent Practices in the Laboratory: Handling and Management of Chemical Hazards</u> The National Academies Press: Washington, DC, 2011).

PLAN carefully and think ahead. You must have an understanding of the intrinsic hazards of the substances being used or potentially formed in any reaction. NEVER work with a reagent you are unfamiliar with without consulting your research advisor or an experienced co-worker *and* relevant SDS information, toxicological data, or other safety information. **Always consider substituting less dangerous substances for hazardous materials and using only the smallest amount possible**. Also, keep in mind that late intermediates, in particular, could be similarly hazardous and should treat them with the same level of caution. For substances with unusual potential hazards, consult A Comprehensive Guide to the Hazardous Properties of Chemical Substances (Patanik, 2007) or the NIOSH website (http://ww.cdc.gov/niosh/npg/). Some of the chemicals under this category are also corrosives, acutely toxic, etc.; please refer to respective SOPs in those cases.

Plan for careful management of the substances through their life cycle—from acquisition and storage through safe disposal. Choose equipment and glassware that are easy to clean and decontaminate. You must also know the signs and symptoms of acute exposure, and know how to respond in an emergency. Document these plans and review them with your research advisor.

Note: The combination of the hazardous effects of two substances may be significantly greater than the toxic effect of either substance alone. Additionally, the possibility of generating toxic reaction products must also be considered during the planning phase.

Never work alone. It is essential that more than one person be present in the lab at all times, but especially when particularly hazarous materials are handled. Additionally, *it is your responsibility to be sure that all individuals working in the vicinity are familiar with the hazards of the experiments that you are conducting* as well as the appropriate emergency responses.

Confine procedures involving particularly hazardous substances that can generate dust, vapors, or aerosols to a chemical hood, glovebox, or other containment device. Procedures such as transfers to reaction vessels should be confined to a designated work area (e.g., fume hood). This area should be recognized as a place where special training/precautions/skill are required. When toxic chemicals are used in a chemical hood, the sash should be at a proper level. When working in a glove box, it should be operated under negative pressure. Post signs to alert others of particularly dangerous experiments.

Wear gloves and safety glasses for protection. Select gloves to make sure they are impervious to the chemical being used and correct thickness.; consult *Prudent Practices* (link above) if you are unsure. Check gloves for integrity and appropriate composition before use. Safety glasses with side shields are a minimum standard. In some cases, face shields or respirators may be required.

Isolate equipment, including vacuum pumps and rotovaps, for handling of particularly hazardous chemicals.

Practice good hygiene. Cleanliness, order and good housekeeping practices create an intrinsically safer workplace. After using particularly hazardous material, wash hands/neck/arms/face with soap and water. Equipment that might be contaminated (including gloves) must not be removed from the area reserved for handling particularly hazardous materials without complete decontamination. Wipe down the immediate work area and equipment to prevent accumulation of chemical residue and thoroughly decontaminate the designated area before resuming normal laboratory work in the area.

Some carcinogens may have specific SOPs that are located in the Appendix or in the laboratory's Safety on Site binder.

NOTE

Any deviation from this SOP requires approval from PI.

Documentation of Training (signature of all users is required)

- Prior to conducting any work with carcinogens, designated personnel must provide training to his/her laboratory personnel specific to the hazards involved in working with this substance, work area decontamination, and emergency procedures.
- The Principal Investigator must provide his/her laboratory personnel with a copy of this SOP and a copy of the SDS provided by the manufacturer.
- The Principal Investigator must ensure that his/her laboratory personnel have attended appropriate laboratory safety training or refresher training within the last one year.

I have read and understand the content of this SOP:

Name	Signature	Date

APPENDIX:

Regulated Carcinogens Used in Lab

????

Appendix V: Strong Corrosives SOP

Standard Operating Procedure

Department:	????
Date SOP written:	????
Date SOP approved by PI/lab supervisor:	????
Principal Investigator:	????
Internal Lab Safety Coordinator/Manager:	????
Lab Phone:	????
Office Phone:	????
Emergency Contact:	????
Location(s) covered by this SOP:	????

Strong Corrosives

Type of SOP:
□ Process □ Hazardous Chemical X Hazardous Class

Purpose

This SOP applies to chemicals that are corrosive to metal, corrosive to skin and corrosive to respiratory tract. A substance or a mixture that by chemical action will materially damage, or even destroy, metals is termed 'corrosive to metal'." Skin corrosion means the production of irreversible damage to the skin following the application of a test substance for up to 4 hours. Substances and mixtures in this hazard class are assigned to a single harmonized corrosion category. These corrosive chemicals can be classified as either acids or bases.

STRONG ACIDS: hydrochloric acid, hydrobromic acid, iodic acid, nitric acid, sulfuric acid, hydrofluoric acid, perchloric acid, acid anhydrides, acid chlorides.

TYPES OF BASES

Ammonium hydroxide, sodium carbonate, calcium hydroxide, sodium hydroxide, potassium hydroxide, alkyl amines, alkoxides, metal amides.

A list of the water reactive chemicals used in this lab is shown in the Appendix at the end of this document.

Physical & Chemical Properties/Definition of Chemical Group

Corrosive compounds have the potential to dissolve organic matter, metals, and other materials. Corrosives may be of any state of matter: liquids, solids, gases, mists or vapors. Commonly used acids are usually liquids, whereas commonly used bases are metal salts. Common corrosive chemicals can also be found as aqueous solutions, and react with water exothermically.

Potential Hazards/Toxicity

Physical Hazards

When corrosive chemicals come into contact with some metals (aluminum, iron, zinc, etc) they have the potential to dissolve or react to evolve flammable H_2 gas. In general, when making aqueous solutions of these compounds, the corrosive chemical should be added to the water as much heat is generated when these solutions are made.

Health Hazards

Compounds under this category can irreversibly damage skin and other tissue.

Personal Protective Equipment (PPE)

Hand Protection

Handle with gloves, Nitrile gloves are recommended.

Eye Protection

ANSI approved properly fitting glasses with side shields. Goggles are recommended. Prescription eye glasses (without side shields) are not adequate protection.

Skin and Body Protection

Flame resistant lab coat preferably made of anti-static material, long pants, and closed-toe shoes

Hygiene Measures

Avoid contact with skin, eyes and clothing. Wash thoroughly and before breaks immediately after handling. Remove contaminated clothing and wash before reuse. Click here to enter text.

Engineering Controls

- Many strong acids generate strong, irritating fumes. A chemical fume hood with exhaust ventilation is required when working with this class of compounds to prevent the build-up of toxic and corrosive gases. The hood sash should be down and serve as a safety shield.
- Corrosive compounds are usually neutralized to biological pH (5-9) before disposal to reduce their corrosive qualities.
- Know where your safety equipment is located (i.e.eye wash/safety shower, and first aid kit).
- Store corrosives in a labeled safety cabinet
- When working with large amounts of strong acids, keep a supply of sodium bicarbonate nearby.

Required Training / Approvals

All work with strong corrosives requires the following prior to beginning work:

- 1.All training must be well documented.
- 2. Must be familiar with the Chemical Hygiene Plan.

3. Must have documented Laboratory Safety Training.

4. Must follow this SOP.

5. Must read the relevant Safety Data Sheet (formerly referenced as Material Safety Data Sheets).

6. Any additional laboratory specific training that is needed to support this SOP must be referenced in the Laboratory Specific Instructions' section and the signed and dated training documents must be uploaded into each assigned researchers training records. Examples include Safety Data Sheets, experimental procedures, journal articles, etc.

7. Must read Prudent Practices in the Laboratory: Handling and Management of Chemical Hazards, Chapter 3.C Toxic Effects of Laboratory Chemicals:

http://www.nap.edu/openbook.php?record_id=4911&page=29

Chapter 5 Working with Chemicals

http://www.nap.edu/openbook.php?record_id=4911&page=79

Administrative Controls

1. Never work alone. At least one other person must be present in the same laboratory when any work involving large amounts of strong corrosives is carried out.

2 .Eliminate or substitute for a less hazardous material when possible.

3. Design your experiment to use the least amount of material possible to achieve the desired result.

4. Verify your experimental set-up and procedure prior to use.

5. Inform colleagues that this material will be used and where.

6. Only use if the area is properly equipped with a certified eye wash/safety shower within ten seconds of travel.

7. Consult with the PI if work involves large quantities.

Storage / Purchasing

It is essential that all strong corrosives be stored separately from all chemicals with which they may react. Ensure secondary containment and segregation of incompatible chemicals per guidance within the Chemical Hygiene Plan. Also, follow any substance-specific storage guidance provided in Safety Data Sheet (SDS) documentation.

The corrosive properties of these materials and their ability to produce fires or explosions by combination with combustible materials make the following considerations mandatory in the selection of a storage site:

-A relatively cool, dry environment free from extremes of temperature/humidity should be maintained.

-Acids and bases should be stored in a manner that separates them from other materials and from each other. Each acid or base should be stored in a manner consistent with its properties. -Stored in material that is acid-resistant; this facilitates flushing and other cleanup procedures in the event of leaks or spills.

-Store on low shelves or in acid/base storage cabinets.

-Segregate oxidizing acids from organic acids, and flammable and combustible liquids.

-Segregate acids from alkali metals such as sodium, potassium, magnesium, etc.

-Use bottle carriers for transporting materials when possible.

-When mixing acids and water, always add acid to water. NEVER add water to acid! -Store solutions of inorganic hydroxides in polyethylene containers.

Acid/Base Baths:

Acid and/or base baths present a serious corrosive hazard and may also present a fire hazard. 1. Preparation, location, use, and disposal all present serious risks and require specific Standard Operating Procedure coverage (PPE, storage, training etc). 2. Emergencies and spills need to be appropriately addressed based on quantities and properties of materials involved.

3. Glassware/labware contaminants must be considered with respect to compatibility with cleaning method.

Before beginning work with chemicals, review the relevant Safety Data Sheet and appropriate chemical safety resources as listed in the Training/Approval section of this document. Develop specific procedures for emergency response and chemical exposure or injury to staff, including any special first aid measures required for the relevant chemical.

First Aid Procedures

If inhaled

Move person into fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Seek medical aid immediately. Send a copy of the MSDS with the victim.

In case of skin contact

Wash skin with soap and water for at least 15 minutes while removing contaminated clothing and shoes

In case of eye contact

Flush eyes with plenty of water for at least 15 minutes. Consult a physician. Send a copy of the MSDS with the victim.

If swallowed

Never give anything by mouth to an unconscious person. Have the person drink water or milk to dilute the corrosive material as soon as possible. Do not induce vomiting. Do not ingest emetics or baking soda. If medical attention must be delayed and the materials are available, drink several ounces of milk of magnesia or other antacids. Send a copy of the MSDS with the victim.

Special Handling and Storage Requirements

Precautions for Handling: Avoid contact with skin, eyes, and clothing. Avoid inhalation.

Conditions for safe storage: Keep container closed in a cool, dry, and well-ventilated area. Store strong corrosives in secondary holding containers. Store acids and bases separately, preferably in a labeled storage cabinet.

Spill and Accident Procedure

Spill – Assess the extent of danger. Help contaminated or injured persons. Ventilate potentially explosive, or corrosive fumes. Do not put water or flammable materials on spill (i.e., paper towels). Avoid putting wet chemicals into a covered container as gas evolution may occur. If acid is spilled, clean the area, wearing gloves, chemical apron, and goggles, and rinse with sodium bicarbonate solution. Do not attempt to handle a large spill. Evacuate the area immediately (you and other researchers in the laboratory) and call for assistance (911, EH&S, and your supervisor). Remain on the scene but at a safe distance to direct response personnel when they arrive.

Small (<1 L) – If you have training, you may assist in the clean-up effort. Use appropriate personal protective equipment and clean-up material for chemical spilled. Double bag spill waste in clear plastic bags, label and take to the next chemical waste pick-up.

Large Chemical Spill (>1 L) Dial 911

Chemical Spill on Body or Clothes – Remove clothing and rinse body thoroughly in emergency shower for at least 15 minutes. Seek medical attention. *Notify supervisor and EH&S immediately*.

Chemical Splash into eyes – Immediately rinse eyeball and inner surface of eyelid with water from the emergency eyewash station for 15 minutes by forcibly holding the eye open. Seek medical attention. *Notify supervisor and EH&S immediately*

Article XI. Medical Emergency Dial 911

a. Life Threatening Emergency, Business Hours, After Hours, Weekends and Holidays – Dial 911 CALL 911 if the condition is LIFE THREATENING or REQUIRES IMMEDIATE MEDICAL ATTENTION.. <u>Note</u>: All serious injuries <u>must</u> be reported to EH&S at x46200 within 8 hours. Complete online incident report at <u>https://www.ehs.uci.edu/apps/hr/index.isp</u>

b. Non-Life Threatening Emergency – Go to the Occupational Health Facility (OHF). After Hours, go to the nearest emergency room. Notify your supervisor or faculty staff if condition is not life threatening.

c. Needle Stick/puncture Exposure (as applicable to chemical handling procedure) – Wash the affected area with antiseptic soap and warm water for 15 minutes. For mucous membrane exposure, flush the affected area for 15 minutes using an eyewash station.

ALL WORK RELATED INJURIES MUST BE REPORTED via the On-line Incident Form <u>https://www.ehs.uci.edu/apps/hr/index.jsp</u> or call Human Resources, Workers Compensation (949) 824-9152.

Decontamination/Waste Disposal Procedure

General hazardous waste disposal guidelines:

Label Waste

 Hazardous waste labels must be placed on the hazardous waste container upon the start of accumulation. Labels are available online at <u>www.ehs.uci.edu/programs/enviro/.</u>

Store Waste

- Hazardous waste containers must be kept closed, except when adding waste.
- Hazardous waste containers must be stored in secondary containment to adequately contain all of the contents of the container.
- Hazardous waste containers must be inspected weekly for signs of leaks, corrosion, or deterioration.
- Be sure that the waste is within biological pH range (pH 5-9)

Dispose of Waste

- Hazardous waste must be transferred to EH&S for disposal within 6 months of being generated.
- Empty Containers: At no time should full or partially full containers be placed in the trash. For more information on empty container management visit <u>www.ehs.uci.edu/programs/enviro/</u>.
- Hazardous Waste Disposal:
 - Visit <u>www.ehs.uci.edu/programs/enviro/</u>.
 - Fill out the "Chemical Waste Collection" form.
 - EH&S will pick up your waste within 1-3 days.

- Do not dispose of chemicals by pouring them down the drain or placing them in the trash.
- Do not use fume hoods to evaporate chemicals.

Safety Data Sheet (SDS) Location

Online SDS can be accessed at http://www.ehs.uci.edu/msds.html.

Lab-Specific Procedures

Lab-specific procedures for this class of chemicals include storing, dispensing, use in chemical reactions, use in processes (e.g., distillation, rotary evaporation, or chromatography), and disposal. Appropriate personal protective equipment and engineering controls are to be used.

NOTE

Any deviation from this SOP requires approval from PI.

Documentation of Training (signature of all users is required)

- Prior to conducting any work with strong corrosives, designated personnel must provide training to his/her laboratory personnel specific to the hazards involved in working with this substance, work area decontamination, and emergency procedures.
- The Principal Investigator must provide his/her laboratory personnel with a copy of this SOP and a copy of the SDS provided by the manufacturer.
- The Principal Investigator must ensure that his/her laboratory personnel have attended appropriate laboratory safety training or refresher training within the last one year.

I have read and understand the content of this SOP:

Name	Signature	Date

APPENDIX:

Strong Corrosives Used in Lab

????

Standard Operating Procedure

Strong Oxidants

Department:	????
Date SOP written:	????
Date SOP approved by PI/lab supervisor:	????
Principal Investigator:	????
Internal Lab Safety Coordinator/Manager:	????
Lab Phone:	????
Office Phone:	????
Emergency Contact:	????
Location(s) covered by this SOP:	????

Type of SOP: □ Process

□Hazardous Chemical

X Hazardous Class

Purpose

This SOP intends to provide general guidance on how to work safely with strong oxidizers. Questions concerning the applicability of any item listed in this procedure should be directed toward the Principal Investigator/Laboratory Supervisor of your laboratory. **Above all, use a combination of common sense and chemical sense.**

A list of the strong oxidants used in this lab is shown in the Appendix at the end of this document.

Physical & Chemical Properties/Definition of Chemical Group

According to *Prudent Practices in the Laboratory: Handling and Management of Chemical Hazards* (section 4.D.3.3 Explosive Hazards, Other Oxidizers) The National Academies Press: Washington, DC, 2011:

An oxidizer "initiates or promotes combustion in other materials, thereby causing fire either of itself or through the release of oxygen or other gases."

Strong oxidizing agents generally create a hazard when combined with other materials, especially organics (fuels) and reducing agents. The NFPA defines four categories of strong oxidizers, divided by the severity of risk when mixed with other compounds:

- Class 1. An oxidizer that does not moderately increase the burn rate of another material.
- Class 2. An oxidizer that will moderately increase the burn rate.
- Class 3. An oxidizer that will cause a severe increase in burn rate.
- Class 4. An oxidizer that has the potential to lead to an explosive oxidation when combined with other materials. *It is recommended to avoid the use of class 4 oxidants;* you must consult your Pl before using a class 4 oxidant.

Class 1. Generally, the anionic component of a salt causes the oxidation. Examples of Class 1 oxidants commonly encountered in a research laboratory setting are metal salts of chromates and dichromates, chlorates and perchlorates, nitrates, peroxides, and perborates. Perchloric acid (below 70% conc.) and hydrogen peroxide (8-27% conc.) are prominent examples of non-salts in this class.

It should also be appreciated that a metal associated with any oxidant may also have toxic or hazardous properties of its own.

The NFPA (<u>http://www.nfpa.org/</u>) list the following as typical Class 1 oxidizers:

(1) All inorganic nitrates (unless otherwise classified)—(Barium nitrate, sodium nitrate)

- (2) All inorganic nitrites (unless otherwise classified)
- (3) Ammonium persulfate
- (4) Barium peroxide
- (5) Calcium hypochlorite (nominal 80%, maximum 81%) blended with magnesium sulfate heptahydrate (nominal 20%, minimum 19%) having an available chlorine of less than or
- equal
 - to 66% and a total water content of at least 17%.
- (6) Calcium peroxide
- (7) Hydrogen peroxide solutions (greater than 8 percent up to 27.5 percent)
- (8) Lead dioxide
- (9) Lithium hypochlorite (39 percent or less available chlorine)
- (10) Lithium peroxide
- (11) Magnesium peroxide
- (12) Manganese dioxide
- (13) Nitric acid (40 percent concentration or less)
- (14) Perchloric acid solutions (less than 50 percent by weight)
- (15) Potassium dichromate
- (16) Potassium percarbonate

Chemical Hygiene Plan

- (17) Potassium persulfate
- (18) Sodium carbonate peroxide
- (19) Sodium dichloro-s-triazinetrione dihydrate (sodium dicholorisocyanurate dihydrate)
- (20) Sodium dichromate
- (21) Sodium perborate (anhydrous)
- (22) Sodium perborate monohydrate
- (23) Sodium perborate tetrahydrate
- (24) Sodium percarbonate
- (25) Sodium persulfate
- (26) Strontium peroxide
- (27) Trichloro-s-triazinetrione [trichloroisocyanuric acid TCCA; trichlor), all physical forms]
- (28) Zinc peroxide

Class 2. Examples in Class 2 oxidants commonly encountered in a research laboratory setting are salts of hypochlorite, permanganate, and peroxide. Examples of non-salts in this class are chromium trioxide, hydrogen peroxide (27-52%), 1,3-dichloro-5,5-dimethylhydantoin (halane), and nitric acid (>70%).

The NFPA (http://www.nfpa.org/) list the following as typical Class 2 oxidizers:

- (1) Barium bromate
- (2) Barium chlorate
- (3) Barium hypochlorite
- (4) Barium perchlorate
- (5) Barium permanganate
- (6) 1-Bromo-3-chloro-5,5-dimethylhydantoin (BCDMH)
- (7) Calcium chlorate
- (8) Calcium chlorite
- (9) Calcium hypochlorite (50% or less by weight)
- (10) Calcium perchlorate
- (11) Calcium permanganate
- (12) Chromium trioxide (chromic acid)
- (13) Copper chlorate
- (14) Halane (1,3-dichloro-5,5-dimethylhydantoin)
- (15) Hydrogen peroxide (greater than 27.5 percent up to 52 percent)
- (16) Lead perchlorate
- (17) Lithium chlorate
- (18) Lithium hypochlorite (more than 39 percent available chlorine)
- (19) Lithium perchlorate
- (20) Magnesium bromate
- (21) Magnesium chlorate
- (22) Magnesium perchlorate
- (23) Mercurous chlorate
- (24) Nitric acid (more than 40 percent but less than 86 percent)
- (25) Nitrogen tetroxide
- (26) Perchloric acid solutions (more than 50 percent but less than 60 percent)
- (27) Potassium perchlorate
- (28) Potassium permanganate
- (29) Potassium peroxide
- (30) Potassium superoxide
- (31) Silver peroxide
- (32) Sodium chlorite (40 percent or less by weight)
- (33) Sodium perchlorate
- (34) Sodium perchlorate monohydrate

- (35) Sodium permanganate
- (36) Sodium peroxide
- (37) Strontium chlorate
- (38) Strontium perchlorate
- (39) Thallium chlorate
- (40) Urea hydrogen peroxide
- (41) Zinc bromate
- (42) Zinc chlorate
- (43) Zinc permanganate

Class 3. Common Class 3 oxidizers encountered in a research laboratory setting are ammonium dichromate, potassium chlorate, hydrogen peroxide (55-91%), calcium hypochlorite, sodium chlorate, perchloric acid (60-72%), sodium chlorite (>40%), and potassium bromate.

The NFPA (<u>http://www.nfpa.org/</u>) list the following as typical Class 3 oxidizers:

- (1) Ammonium dichromate
- (2) Calcium hypochlorite (over 50% by weight)
- (3) Chloric acid (10 percent maximum concentration)
- (4) Hydrogen peroxide solutions (greater than 52 percent up to 91 percent)
- (5) Mono-(trichloro)-tetra-(monopotassium dichloro)-penta-s-triazinetrione
- (6) Nitric acid, fuming (more than 86 percent concentration)
- (7) Perchloric acid solutions (60 percent to 72 percent by weight)
- (8) Potassium bromate
- (9) Potassium chlorate
- (10) Potassium dichloro-s-triazinetrione (potassium dichloroisocyanurate)
- (11) Sodium bromate
- (12) Sodium chlorate
- (13) Sodium chlorite (over 40 percent by weight)
- (14) Sodium dichloro-s-triazinetrione anhydrous (sodium dichloroisocyanurate anhydrous)

Class 4. Common Class 4 oxidizers encountered in a research laboratory setting include ammonium perchlorate, ammonium permanganate, guanidine nitrate, hydrogen peroxide (>92%), perchloric acid (>72%), and potassium superoxide. *Avoid the use of class 4 oxidants; you must consult your PI before using a class 4 oxidant.*

The NFPA (http://www.nfpa.org/) list the following as typical Class 4 oxidizers:

(1) Ammonium perchlorate (particle size greater than 15 microns; **less than 15 microns is classified as**

an explosive and, as such, is not covered by this code)

- (2) Ammonium permanganate
- (3) Guanidine nitrate
- (4) Hydrogen peroxide solutions (greater than 91 percent)
- (5) Tetranitromethane

Potential Hazards/Toxicity

Physical Hazards

Strong oxidizing agents can present fire and explosive hazards. This hazard is highest when there is a possibility of an oxidizing agent coming in contact with a reducing agent, a fuel, or some other combustible.

According to *Prudent Practices in the Laboratory: Handling and Management of Chemical Hazards* (section 4.D.3.3 Explosive Hazards, Other Oxidizers) The National Academies Press: Washington, DC, 2011.

"Oxidizing agents may react violently when they come into contact with reducing materials and sometimes with ordinary combustibles. Such oxidizing agents include halogens, oxyhalogens and organic peroxyhalogens, chromates, and persulfates as well as peroxides. Inorganic peroxides are generally stable. However, they may generate organic peroxides and hydroperoxides in contact with organic compounds, react violently with water (alkali metal peroxides), and form superoxides and ozonides (alkali metal peroxides). Perchloric acid is a powerful oxidizing agent with organic compounds and other reducing agents.

Perchlorate salts are explosive and should be treated as potentially hazardous compounds."

HEALTH HAZARDS

Many compounds under this category are toxic. An SDS should be consulted for toxicological information prior to using any particular oxidizing agent. Other common hazards may include corrosively and peroxide formation.

Personal Protective Equipment (PPE)

Hand Protection

Handle with gloves. Nitrile gloves are generally suitable for milder oxidants. Remember that many organic solvents will quickly permeate most types of gloves, including nitrile. Should material come in contact with gloves, dispose of glove immediately unless the glove is known to be impermeable to the material or solvents involved. Never reuse disposable gloves.

NOTE: Consult with your preferred glove manufacturer to ensure that the gloves you plan on using are compatible with specific oxidants. Refer to glove selection chart from any of the various links below:

http://www.ansellpro.com/download/Ansell_8thEditionChemicalResistanceGuide.pdf

http://www.allsafetyproducts.biz/page/74172

http://www.showabestglove.com/site/default.aspx

http://www.mapaglove.com/

Eye Protection

ANSI approved tight-fitting safety glasses with side shields. Goggles are required when there is the potential for splashes. When appropriate or desired, use a face shield. Prescription eyeglasses (without side slides) are **not** adequate protection.

Skin and Body Protection

Flame resistant lab coat, preferably made of antistatic material (e.g., Nomex®), with sleeves fully extended and coat buttoned. **Non-synthetic clothing**, long pants, and closed-toe shoes must be worn.

Hygiene Measures

Avoid contact with skin, eyes and clothing. Wash hands before breaks and immediately after handling the product.

Respiratory Protection

Generally a chemical fume hood will provide adequate respiratory protection. The Chemical Hygiene Officer must be consulted if there is further risk of inhalation exposure. Additional appropriate PPE may be required if procedures or processes present additional risk.

Engineering Controls

Control, contain, and minimize the amount of oxidizers.

The following is a general plan for all strong oxidizers:

Always use strong oxidizers in a certified chemical fume hood to minimize the potential for the spread of a fire if one should occur. Ensure that adequate space is available in the hood to perform the work. Avoid placing solvent squirt bottles in close proximity to the reaction, and avoid having excess flammable material (kimwipes, paper towels, etc) in the hood. Have a fire extinguisher with current inspection tag at hand (not just hanging on the wall in a distant part of the laboratory) when working with Class 2-4 materials. It is recommended to avoid the use of Class 4 oxidizers. If no alternative is available, then operations **MUST** be carried out in a fume hood with the addition of a blast shield. No part of the body (for example, hands) should ever be directly exposed to these materials when they are mixed with other chemicals.

Perchloric acid has a notorious history of causing unanticipated explosions. Perchloric acid can form explosive salts almost anywhere, including in the exhaust ducts of fume hoods, soiled laboratory benches, and even trace metallic residues on the inside of reaction flasks. Many perchlorate salts are shock sensitive and can lay dormant for very long periods. For these reasons, it is imperative that perchloric acid only be used in a perchloric acid designated fume hood that is not used for any other function. Spills should be immediately and thoroughly cleaned up. This fume hood shall be prominently marked as for use ONLY with perchloric acid and not other materials. EH&S should be contacted for proper signage and approvals. Keep in mind that only a new fume hood can be designated for perchloric acid use.

Required Training / Approvals

All work with strong oxidizers requires the following prior to beginning work:

- 1. All use of Class 3 or 4 oxidants must be pre-approved by the Principal Investigator prior to use and all training must be well documented.
- 2. Must be familiar with the Chemical Hygiene Plan.
- 3. Must have documented Laboratory Safety Principles/IIPP training.
- 4. Must follow this SOP.
- 5. Must read the relevant Safety Data Sheet (formerly referenced as Material Safety Data Sheets).

- 6. Environment, Health and Safety must be consulted in advance if any work involves the heating of
 - perchloric acid.
- 7. Must read Prudent Practices in the Laboratory: Handling and Management of Chemical Hazards (section 3.D.2.3 3.D.3.3 Incompatible Chemicals Other Oxidizers) http://www.nap.edu/openbook.php?record_id=4911&page=51
- 8. Any additional laboratory specific training required to support this SOP must be referenced in the Laboratory Specific Instructions section and the signed and dated training documents must be uploaded into each assigned researcher's training records. Examples include Safety Data Sheets, experimental procedures, journal articles, etc.

Administrative Controls

- 1. Never work alone. At least one other person must be present in the same laboratory when any work involving strong oxidizers is involved.
- 2. Eliminate or substitute for a less hazardous material when possible.

3. Design your experiment to use the least amount of material possible to achieve the desired result.

- 4. Verify your experimental set-up and procedure prior to use.
- 5. Inform colleagues this material will be used and where.
- 6. Only use if the area is properly equipped with a certified eye wash and safety shower within ten seconds of availability.
- 7. Consult with the PI if work involves large quantities.

Storage / Purchasing

It is essential that all strong oxidants be stored separately from all chemicals with which they may react [i.e., reductants and fuel sources (organic compounds)]. Do not store oxidizers in the same unit as flammables. Ensure secondary containment and segregation of incompatible chemicals per guidance within the Chemical Hygiene Plan. Also, follow any substance-specific storage guidance provided in Safety Data Sheet (SDS) documentation.

First Aid Procedures

Before beginning work with chemicals, review the relevant Safety Data Sheet and appropriate chemical safety resources as listed in the Training/Approval section of this document. Develop specific procedures for emergency response and chemical exposure or injury to staff, including any special first aid measures required for the relevant chemical.

Additional special instructions for Department of Chemistry / Biochemistry personnel only:

- Report serious incidents immediately: Call 9-1-1
- Immediately secure any incident scene from all access and preserve all evidence for no less than 24 hours.

If inhaled

Move into fresh air immediately and provide oxygen. If not breathing give artificial respiration. Seek medical attention immediately.

In case of skin contact

Immediately flush skin with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Discard or thoroughly wash any contaminated clothing and shoes before reuse. Seek medical attention at the first sign of any adverse symptoms.

In case of eye contact

Check for and remove any contact lenses. Rinse thoroughly with plenty of water for at least 15 minutes and consult a physician. Seek immediate medical attention and continue eye rinse during transport to hospital.

If swallowed

Do NOT induce vomiting unless directed by medical personnel. Never give anything by mouth to an unconscious person. Seek medical attention immediately.

Special Handling and Storage Requirements

Precautions for safe handling: Avoid contact with skin and eyes. Avoid inhalation of vapor, mist, or dust. Avoid formation of dust whenever possible.

Conditions for safe storage: Avoid exposure to water, moisture, or humid environment; oxidizers may react violently with moisture. Store container tightly closed in a cool, dry, and well ventilated place. Keep away from incompatible materials and conditions (fuel sources, reducing agents, organic materials) using secondary containment or, ideally, in separate storage room. Protect from sunlight.

It is essential that all strong oxidants be stored separately from all chemicals with which they may react [i.e., reductants and fuel sources (organic compounds)]. Do not store oxidizers in the same unit as flammables. Ensure secondary containment and segregation of incompatible chemicals per guidance within the Chemical Hygiene Plan. Also, follow any substance-specific storage guidance provided in Safety Data Sheet (SDS) documentation.

Spill and Accident Procedure

Spill – Assess the extent of danger. Help contaminated or injured persons if safe to do so. Evacuate the spill area. Avoid breathing vapors. If you are uncomfortable with the extant of danger, contact your P.I. and EH&S. Dial 911 if the extent of danger constitutes an imminent risk to human health. If possible, confine the spill to a small area using a spill kit or absorbent material. Keep others from entering contaminated area (e.g., use caution tape, barriers, etc.).

Small (<100 g)

Assess the extent of danger. If you are uncomfortable with the risk, contact EH&S and your PI. If you have had training and you are comfortable doing so, you may assist in the clean-up effort. Use appropriate personal protective equipment and clean-up materials for chemical spilled. Double bag waste in clear plastic bags or approved container(s), label and contact EH&S for hazardous waste cleanup.

Large (>100 g)

Dial 911 and EH&S at x46200 for assistance.

Chemical Spill on Body or Clothes

Remove clothing and rinse body thoroughly in emergency shower for at least 15 minutes. Seek immediate medical attention if any symptoms appear. *Notify supervisor and EH&S at x46200 immediately.*

Chemical Splash Into Eyes

Immediately rinse eyeball and inner surface of eyelid with water from the emergency eyewash station for 15 minutes by forcibly holding the eye open. Seek immediate medical attention. *Notify supervisor and EH&S at x46200 immediately.*

Article XII.

Article XIII. Medical Emergency Dial 911

a. Life Threatening Emergency, Business Hours, After Hours, Weekends and Holidays – Dial 911 if the condition is LIFE THREATENING or REQUIRES IMMEDIATE MEDICAL ATTENTION.. <u>Note</u>: All serious injuries <u>must</u> be reported to EH&S at **x46200** within 8 hours. Complete online incident report at <u>https://www.ehs.uci.edu/apps/hr/index.jsp</u>

b. Non-Life Threatening Emergency – Notify your supervisor or faculty staff if condition is not life threatening.

c. Needle Stick/puncture Exposure – Wash the affected area with antiseptic soap and warm water for 15 minutes. For mucous membrane exposure, flush the affected area for 15 minutes using an eyewash station. Seek immediate medical attention if any symptoms appear.

ALL WORK RELATED INJURIES MUST BE REPORTED via the On-line Incident Form https://www.ehs.uci.edu/apps/hr/index.jsp or call Human Resources, Workers Compensation (949) 824-9152.

Decontamination/Waste Disposal Procedure

Decontamination of Equipment

• Equipment that needs to be decontaminated (for repair or change of location etc.) must be washed with soapy water and rinsed with copious amounts of water.

Hazardous waste containing oxidizers

• Hazardous waste containing oxidizers should be segregated from other hazardous waste streams. Contact EH&S for a pickup of hazardous waste containing oxidizers.

General hazardous waste disposal guidelines

Label Waste

• Hazardous waste labels must be placed on the hazardous waste container upon the start of accumulation. Labels are available online at www.ehs.uci.edu/programs/enviro/.

Store Waste

- Hazardous waste containers must be kept closed, except when adding waste.
- Hazardous waste containers must be stored in secondary containment to adequately contain all of the contents of the container.
- Hazardous waste containers must be inspected weekly for signs of leaks, corrosion, or deterioration.

Dispose of Waste

- Hazardous waste must be transferred to EH&S for disposal within 6 months of being generated.
- Empty Containers: At no time should full or partially full containers be placed in the trash. For more information on empty container management visit <u>www.ehs.uci.edu/programs/enviro/</u>.
- Hazardous Waste Disposal:
 - Visit <u>www.ehs.uci.edu/programs/enviro/</u>.
 - Fill out the "Chemical Waste Collection" form.
 - EH&S will pick up your waste within 1-3 days.
- Do not dispose of chemicals by pouring them down the drain or placing them in the trash.
- Do not use fume hoods to evaporate chemicals.

Safety Data Sheet (SDS) Location

MSDSs can be found online at the UCI EH&S web site (<u>http://www.ehs.uci.edu/msds.html</u>).

Designated Area

As noted above, experiments involving highly toxic chemicals should be confined to a designated work area (e.g., fume hood). This area should be recognized as a place where special training, precautions, or skill are required. Where appropriate, post signs to designate these areas and alert others of particularly dangerous experiments. If Perchloric acid is to be used as an oxidant, a designated area must be established.

Prior Approval Required

Class 4 oxidizers cannot be used without prior approval from the PI. Additionally, less experienced persons should consult their (or designee) and coworkers when working with class 2 or 3 oxidizers for the first time.

Lab-Specific Procedures

Lab-specific procedures for this class of chemicals include storing, dispensing, use in chemical reactions, use in processes (e.g., distillation, rotary evaporation, or chromatography), and disposal. Appropriate personal protective equipment and engineering controls are to be used.

- Consult an SDS, your PI, and knowledgeable coworkers prior to using strong oxidizers for the first time.
- Don proper PPE (see above), including a flame retardant lab coat, before using strong oxidizers.
- Work with strong oxidizers in an operative chemical fume hood.
- Ensure that the work space is free of incompatible materials, especially reducing agent.
- Use a blast shield when working with class 4 strong oxidizer (class 4 strong oxidizers cannot be used without prior approval of your PI.
- Ensure that hazardous waste containing strong oxidizers is put in a segregated waste stream.

Concentrated hydrogen peroxide is a strong oxidizer; avoid contact of hydrogen peroxide with organics and metals. Read appropriate safety instructions before working with concentrated hydrogen peroxide. Do not make more than 25 mL of the 90% hydrogen peroxide at a time. Store sample in 50 mL brown plastic bottle to shield from light. Use parafilm to seal mouth of container. This will provide sufficient barrier to prevent contamination of the sample, yet provide a relief outlet for potential pressure build up inside the bottle. Use no more than 5-10 mL of the 90% sample during an experiment. Wear eye protection and gloves (see PPE section) while handling and transferring 90% hydrogen peroxide. Avoid contact with skin. If contact occurs, wash with plenty of water. Report any safety incidents immediately to PI.

Perchloric acid has a notorious history of causing unanticipated explosions. Perchloric acid can form explosive salts almost anywhere, including in the exhaust ducts of fume hoods, soiled laboratory benches, and even trace metallic residues on the inside of reaction flasks. Many perchlorate salts are shock sensitive and can lay dormant for very long periods. For these reasons, it is imperative that perchloric acid only be used in a perchloric acid designated fume hood that is not used for any other function. Spills should be immediately and thoroughly cleaned up. This fume hood shall be prominently marked as for use ONLY with perchloric acid and not other materials. EH&S should be contacted for proper signage and approvals. Keep in mind that only a new fume hood can be designated for perchloric acid use.

NOTE

Any deviation from this SOP requires approval from PI.

Documentation of Training (signature of all users is required)

- Prior to conducting any work with strong oxidizing agents, designated personnel must provide training to his/her laboratory personnel specific to the hazards involved in working with this substance, work area decontamination, and emergency procedures.
- The Principal Investigator must provide his/her laboratory personnel with a copy of this SOP and a copy of the SDS provided by the manufacturer.
- The Principal Investigator must ensure that his/her laboratory personnel have attended appropriate laboratory safety training or refresher training within the last one year.

Name Signature Date

I have read and understand the content of this SOP:

APPENDIX:

Strong Oxidant Chemicals Used in Lab

????

Appendix X: Strong Reducing Agents

Standard Operating Procedure

Strong Reducing Agents

Department:	????
Date SOP written:	????
Date SOP approved by PI/lab supervisor:	????
Principal Investigator:	????
Internal Lab Safety Coordinator/Manager:	????
Lab Phone:	????
Office Phone:	????
Emergency Contact:	????
Location(s) covered by this SOP:	????

Type of SOP:
□ Process □ Hazardous Chemical X Hazardous Class

Purpose

This standard operating procedure is intended to cover the safe storage, handling, and use of strong reducing agents.

Strong reducing agents can react violently with air and/or water and as such precautions should be taken to exclude air and water from the reagent (See also the SOPs for pyrophoric and water reactive chemicals). Exposure of strong reducing agents to water generates hydrogen gas, which can lead to high pressures and potential explosions. Procedures should be chosen carefully to quench excess reagents in a safe manner. Examples of work-up procedures for selected reagents are listed below. Improper work-up procedures are a common cause of accidents when dealing with these reagents.

A list of the water reactive chemicals used in this lab is shown in the Appendix at the end of this document.

Required Training / Approvals

All work with strong reducing agents requires the following prior to beginning:

- All training must be well documented.
- Must be familiar with the Chemical Hygiene Plan.
- Must have documented Laboratory Safety training (IIPP).
- Must follow this SOP.
- Must read the relevant Safety Data Sheet (SDS, formerly referenced as Material Safety Data Sheets or MSDS).
- Must read Prudent Practices in the Laboratory: Handling and Management of Chemical Hazards - <u>http://www.nap.edu/catalog.php?record_id=12654</u>
- Any additional laboratory specific training needed to support this SOP must be referenced in the Laboratory Specific Instructions section and the signed and dated training documents must be uploaded into each assigned researchers training records. Examples include Safety Data Sheets, experimental procedures, journal articles, etc.
- Staff must have been trained and demonstrate proficiency in handling strong reducing agents.

BEFORE working with a strong reducing agent for the first time, users must:

- Discuss with your PI or an experienced coworker before using a strong reducing agent for the first time.
- Read the relevant Material Safety Data Sheets (MSDS), technical bulletins, and guidance documents to understand and how to mitigate the hazards. The MSDS must be reviewed before using an unfamiliar chemical and periodically as a reminder.
- Be familiar with this SOP and identify the safety precautions specific to the operations (<u>http://www.ehs.uci.edu/labres.html</u>)
- Consider performing a "dry run" to identify and resolve possible hazards before conducting the actual procedure.
- Users of strong reducing agents must be trained in proper lab technique and be able to demonstrate proficiency.
- Use less toxic or hazardous substances in your experiment and minimize the amount of hazardous waste generated.
- Perform a hazard analysis and identify the failure modes in your experiment. Be prepared to handle accidents.
- Complete required EH&S safety training requirements (<u>www.ted.uci.edu</u>) and lab specific training. Address all Safety on site (SOS) issues.

It is the Principal Investigators responsibility to ensure activity specific laboratory procedures and/or processes are taken into account when using this SOP. This SOP is intended to provide general guidance on how to safely work with strong reducing agents. The reactivity of these reagents varies and should be evaluated together with the Principal Investigator/Laboratory Supervisor. If you have questions concerning the applicability of any item listed in this procedure, contact the Principal Investigator/Laboratory Supervisor of your laboratory.

Physical & Chemical Properties/Definition of Chemical Group

Strong reducing agents often react violently with air and/or water.

Some Examples of Strong Reducing Agents

- Sodium borohydride (NaBH₄)
- Sodium cyanoborohydride (NaBH₃CN)
- Lithium aluminum hydride (LiAlH₄ or LAH)
- Diisobutylaluminum hydride (DIBAL)
- Sodium (Na) or potassium (K) metal
- Potassium graphite (KC₈)
- Alkali metal naphthylide (MC₁₀H₈) or anthracenide (MC₁₄H₁₀)

A more extensive list of pyrophoric compounds can be found in Bretherick's *Handbook of Reactive Chemical Hazards*

Potential Hazards/Toxicity

Strong reducing agents are highly corrosive and react violently with water, generating flammable gases. In particular, sodium cyanoborohydride can generate hydrogen cyanide gas when exposed to water. These reagents are also flammable, both in the solid form and in a solution.

Hazard Identification Resources:

Safety Data Sheet resources at<u>http://www.ehs.uci.edu/msds.html</u> Risk Assessment Tool at<u>http://www.ehs.uci.edu/programs/labres/LABRAT.pdf</u> High Hazard Chemicals/Process Screening Tool at<u>High Hazard</u> <u>Chemicals/Processes Screening Tool</u>

Personal Protective Equipment (PPE)

Ensure that all lab personnel have completed and reviewed the PPE assessment tool.

Eye Protection

- Chemical splash goggles or safety glasses that meet the ANSI Z.87.1 1989 standard must be worn whenever handling pyrophoric chemicals. Ordinary prescription eyeglasses will NOT provide adequate protection. When there is the potential for splashes, goggles must be worn, and when appropriate, a face shield for added protection.
- A face shield, worn over safety eyewear, is required any time there is a risk of explosion, large splash hazard, or a highly exothermic reaction. All manipulations of strong reducing agents that pose this risk should be carried out in a fume hood with the sash in the lowest feasible position.

Skin Protection

• Gloves must be worn when handling strong reducing agents. Be sure to use adequate protection to prevent skin exposures. Sigma-Aldrich recommends the use of nitrile gloves underneath neoprene gloves. Flame retardant gloves should be used for handling

large quantities of these chemicals.

NOTE: Consult with your preferred glove manufacturer to ensure that the gloves you plan on using are compatible with the reducing agent you are using.

Refer to glove data at the websites listed below: <u>http://www.ansellpro.com/download/Ansell_8thEditionChemicalResistanceGuide.pdf</u> <u>http://www.allsafetyproducts.biz/page/74172</u> <u>http://www.showabestglove.com/site/default.aspx</u> <u>http://www.mapaglove.com/</u>

- A lab coat made from fire retardant material is recommended for labs using these reagents routinely. Lab coats need to be buttoned and fit properly to cover as much skin as possible.
- Appropriate shoes that cover the entire foot (closed toe, closed heel, no holes in the top) and long pants must be worn.
- No synthetic clothing

Respirator Protection

Respiratory protection is generally not required for lab research, provided the appropriate engineering controls are employed. Respirators should be used only under any of the following circumstances:

- As a last line of defense (i.e., after engineering and administrative controls have been exhausted).
- When Permissible Exposure Limit (PEL) has exceeded or when there is a possibility that PEL will be exceeded.
- Regulations require the use of a respirator.
- An employer requires the use of a respirator.
- There is potential for harmful exposure due to an atmospheric contaminant (in the absence of PEL)
- As PPE in the event of a chemical spill clean-up process

Lab personnel intending to use/wear a respirator mask must be trained and fit-tested by EH&S. This is a regulatory requirement. If you think that your process may require respirator use, contact EH&S for assistance (<u>http://www.ehs.uci.edu/programs/ih/respiratory.html</u>)

Engineering Controls

Have the proper equipment and the emergency phone number (9-1-1) readily available for any

emergencies. A small beaker of dry sand or soda ash (lime) in the work area is useful to extinguish any small fire that occurs at the syringe tip and to receive any last drops of reagent from the syringe.

Eyewash/ Safety Shower

• A combination eyewash/safety shower should be within 10 seconds travel time where strong reducing agents are used. Inside the laboratory is optimum. Bottle type eyewash stations are not acceptable.

Fume Hood

- Verify that your fume hood has been checked in the last 12 months.
- All work with strong reducing agents should be performed in a clean, working chemical fume hood. Ensure that adequate space is available in the hood to perform the work. Avoid placing solvent squirt bottles in close proximity to the reaction, and avoid having excess flammable material (kimwipes, paper towels, etc) on the floor of the hood.
- As much as possible, it is preferable to use keep strong reducing agents towards the back of the fume hood with sash in the lowest feasible position.

Safety shielding

• Safety shielding is required any time there is a risk of explosion, splash hazard or a highly exothermic reaction. Portable shields may be used to provide additional protection.

Glove (dry) box

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

Inert atmosphere manifold (Schlenk Line)

• Nitrogen or argon lines are extremely useful when performing manipulations of air and/or water sensitive reagents. If a glove box cannot be used, proper use of an inert atmosphere manifold can help minimize exposure of these reagents to air and water.

First Aid Procedures

Before beginning to work with strong reducing agents, review the relevant Material Safety Data Sheet (MSDS) and appropriate chemical safety resources as listed in the Training/Approval section of this document. Develop specific procedures for emergency response and chemical exposure or injury to staff, including any special first aid measures required for the relevant chemical.

Additional special instructions for Department of Chemistry / Biochemistry personnel only:

- Report serious incidents immediately: Call 9-1-1
- Immediately secure any incident scene from all access and preserve all evidence for no less than 24 hours.

Chemicals may enter the body through four routes: inhalation, ingestion, injection, or contact with the skin and eyes. With each route of exposure, the likelihood of injury depends on the

toxicity of the chemical involved, the concentration of the material, and the duration of contact. For all exposures:

- Seek immediate medical attention.
- Call Campus Police at 911 and request an ambulance if transportation is necessary.
- Call the Poison Control System, (800) 222-1222, if additional information is needed.
- If you're injured, experience a hazardous material exposure, or develop a job-related illness as a result of chemical exposure, seek medical treatment immediately.

Special Handling and Storage Requirements

Strong reducing agents can be handled and stored safely provided exposure to atmospheric oxygen and moisture is avoided.

Some strong reducing agents cannot be stored in unsprinklered buildings; check list of restricted chemicals at:

http://www.ehs.uci.edu/programs/fire/ChemicalsNotPermittedInUnsprinkleredBuildings.pdf

- Purchase, use, and store minimal amounts of strong reducing agents.
- Do not store strong reducing agents with flammable materials or in a flammable liquids storage cabinet. Containers carrying strong reducing agents must be clearly labeled with the correct chemical name, in English, and hazard warning.
- Store as recommended in the MSDS. A nitrogen-filled desiccator or glove box is a suitable storage location.

• If strong reducing agents are received in a specially designed shipping, storage or dispensing container, (such as the Aldrich Sure/Seal packaging system) ensure that the integrity of that container is maintained.

• Ensure that sufficient protective solvent, oil, kerosene, or inert gas remains in the container while the material is stored.

• NEVER return excess chemical to the original container. Small amounts of impurities introduced into the container may cause a fire or explosion.

- For storage of excess chemical, prepare a storage vessel in the following manner:
 - Dry a new empty containers thoroughly
 - Select a septum that fits snugly into the neck of the vessel
 - Insert septum into neck in a way that prevents atmosphere from entering the clean, dry (or reagent filled) flask.

• Insert a needle to inject inert gas and to maintain a blanket of dry, inert gas above the reactive reagent through and quickly insert a second needle to vent the flask.

• Once the vessel is fully purged with inert gas, remove the vent needle and add the reagent carefully then remove the gas line.

• For long-term storage, the septum should be secured with a copper wire.

Spill and Accident Procedure

• A container of powdered lime or dry sand, which may be adequate to smother a small spill that might occur, should be kept within arm's reach when working with strong reducing agents.

- **DO NOT** use water on a strong reducing agent fire, as it can make the incident even worse.
- Do not use combustible materials like paper towels to clean up a spill, as these may increase the risk of ignition with a a strong reducing agent. Soda ash (powdered lime) or dry sand may cover and contain any small spill that occurs.
- The recommended fire extinguisher is a standard dry powder (ABC) type and should be within immediate reach in the event of an incident.
- Class D extinguishers are recommended for combustible solid metal fires (e.g, sodium, LAH), but not for organolithium reagents.

Note: If a small amount of reducing agent in solid form has spilled, carefully collect the material into a beaker, and quench the reagent in a ventilated fume hood. For larger spills contact EH&S.

Chemical Spill

Spill – Assess the extent of danger. Help contaminated or injured persons if safe to do so. Evacuate the spill area. Avoid breathing vapors. If possible, confine the spill to a small area using a spill kit or absorbent material. Keep others from entering contaminated area (e.g., use caution tape, barriers, etc.).

Small (<100 g) – Even small spills of a pyrophoric material, especially liquids, can be extremely hazardous, especially if other flammable compounds or solvents are in the lab or fume hood. If the fire can be readily contained and you have had training, you may assist in the clean-up effort. Use appropriate personal protective equipment and clean-up materials for chemical spilled. Double bag neutralized waste in clear plastic bags or approved container(s), label and take to the next chemical waste pick-up.

Large (>100 g) – Dial 911 and EH&S at x4-6200 for assistance.

Chemical Spill on Body or Clothes – Remove clothing and rinse body thoroughly in emergency shower for at least 15 minutes. Seek medical attention. *Notify supervisor and EH&S at x4-6200 immediately.*

Chemical Splash Into Eyes – Immediately rinse eyeball and inner surface of eyelid with water from the emergency eyewash station for 15 minutes by forcibly holding the eye open. Seek medical attention. *Notify supervisor and EH&S at x4-6200 immediately*.

Article XIV.

Article XV. Medical Emergency

a. Life Threatening Emergency – Dial 911 if the condition is LIFE THREATENING or REQUIRES IMMEDIATE MEDICAL ATTENTION.

b. Non-Life Threatening Emergency– Notify your supervisor or faculty staff if condition is not life threatening.

c. Needle Stick/punctureExposure (as applicable to chemical handling procedure) – Wash the affected area with antiseptic soap and warm water for 15 minutes. <u>For mucous</u> <u>membrane exposure</u>, flush the affected area for 15 minutes using an eyewash station.

All serious injuries <u>must</u> be reported to EH&S at **x4-6200** within 8 hours.

ALL WORK RELATED INJURIES MUST BE REPORTED via the On-line Incident Form <u>https://www.ehs.uci.edu/apps/hr/index.jsp</u> or call Human Resources, Workers Compensation (949) 824-9152.

Decontamination/Waste Disposal Procedure

Disposal of Strong Reducing Agents

- A container with any residue of strong reducing agents should never be left open to the atmosphere.
- Unused or unwanted strong reducing agents must be destroyed by transferring the materials to an appropriate reaction flask under inert atmosphere for hydrolysis and/or neutralization with adequate cooling.
- To the flask should be added an inert dry solvent, such as toluene or THF, to dilute the reactive reagent under an atmosphere of dry nitrogen or argon.
- The stirred solution should be neutralized by the drop-wise addition of a ice-chilled protic solvent, such as isopropyl alcohol. **Never** add water or a protic solvent **directly to** a strong reducing agent.
- Before disposal, the flow of inert gas should be stopped to expose the quenched solution to the ambient atmosphere for a 24-hour period at which time standard waste disposal practices can be followed.
- Once emptied, the flask should then be triple rinsed with isopropyl alcohol and left to dry in the back of a fume hood.
- The original container should be triple-rinsed with a dry inert solvent under a flow of inert gas. These washings should then be treated as described above. The triple-rinsed container should be left open in back of a hood exposed to the ambient atmosphere for at least a week to ensure all remaining residue has been quenched. After a week, the container should then be triple rinsed again with isopropyl alcohol.

Disposal of Materials Contaminated with Strong Reducing Agents

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

General hazardous waste disposal guidelines

Label Waste

• Hazardous waste labels must be placed on the hazardous waste container upon the start of accumulation. Labels are available online at www.ehs.uci.edu/programs/enviro/.

Store Waste

- Hazardous waste containers must be kept closed, except when adding waste.
- Hazardous waste containers must be stored in secondary containment to adequately contain all of the contents of the container.

 Hazardous waste containers must be inspected weekly for signs of leaks, corrosion, or deterioration.

Dispose of Waste

- Hazardous waste must be transferred to EH&S for disposal within 6 months of being generated.
- Empty Containers: At no time should full or partially full containers be placed in the trash. For more information on empty container management visit www.ehs.uci.edu/programs/enviro/.
- Hazardous Waste Disposal: visit <u>www.ehs.uci.edu/programs/enviro/</u>.
- Fill out the "Chemical Waste Collection" form.
- EH&S will pick up your waste within 1-3 days.
- Do not dispose of chemicals by pouring them down the drain or placing them in the trash.
- Do not use fume hoods to evaporate chemicals.

Safety Data Sheet (SDS) Location

Online SDS can be accessed at http://www.ehs.uci.edu/msds.html.

Lab-Specific Procedures

Lab-specific procedures for this class of chemicals include storing, dispensing, use in chemical reactions, use in processes (e.g., distillation, rotary evaporation, or chromatography), and disposal. Appropriate personal protective equipment and engineering controls are to be used.

Use of sodium metal (adapted from an SOP from Stony Brook University, available at http://naples.cc.sunysb.edu/Admin/HRSForms.nsf/pub/EHSD0433):

- Sodium is a potent reducing agent and reacts violently with water to form hydrogen and sodium hydroxide.
- Sodium reacts violently and with the release of heat upon contact with mineral acids, halogens, oxidizing agents, organic and inorganic halides, and protic media.
- Mixtures of sodium and halogenated solvents can explode violently.
- Sodium also reacts with halogenated hydrocarbons such as carbon tetrachloride and chloroform, sulfur oxides, and phosphorous to generate shock-sensitive product mixtures.
- Sodium dissolves in many other metals such as mercury and potassium to form amalgams, releasing large amounts of heat.
- Metals like sodium become more reactive as the surface area of the particles increases. Thus, reactions involving large pieces of sodium metal (especially those with some oxide or hydroxide coating) may be slow and controlled, but similar reactions involving clean, high-surface-area sodium dispersions may be vigorous or violent. 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.

• All equipment used to cut or handle sodium must be bone dry and free of all water moisture before use. All equipment and work surfaces must be thoroughly cleaned and decontaminated with isopropanol before storage or reuse.

Quenching excess sodium:

- Waste scraps of sodium should quenched in the lab shortly rather than returning them to the original container. This waste must also be disposed of as hazardous waste by giving it to EH&S. Only properly trained lab staff are allowed to quench sodium metal.
- The quenching of sodium metal waste must be done in the hood since hydrogen gas is generated. All flammable materials must be removed from the fume hood prior to beginning this procedure.
- Using tweezers, add the scraps of sodium to 95% ethanol in an Erlenmeyer flask at such a rate that the solvent does not boil.
- Generally, use about 200 mL of ethanol for each gram (estimated) of sodium. If a large amount of material (more than a few grams; large chunks should be cut into small pieces) is involved it is a good idea to put the flask in a secondary container like a crystallizing dish or a metal pan.
- Once the sodium has visually reacted, add water in small quantities (about 0.5 mL at a time) while swirling the flask to get good mixing until there is a clear solution.
 - This step is important. When sodium reacts with ethanol it forms sodium ethoxide which has a tendency to form a gel with ethanol. Free sodium metal can remain unreacted and undetected in this gel for long periods of time. Adding water in a controlled fashion converts the sodium ethoxide to sodium hydroxide, which is soluble in the ethanol-water mixture and also decomposes any residual sodium.
- The quenched waste solution should be put in a bottle and labeled as sodium hydroxide in water-ethanol and given to EH&S for disposal.

Lithium Aluminum Hydride Reactions

"Warning on the use of aluminum lithium hydride (LAH): Following the investigation of a laboratory explosion, Dr. M. L H. Green of the University of Oxford has warned that the following precautions are essential for the safe use of lithium aluminum hydride (LAH). The measures are to prevent overheating of the hydride and dissociation to finely divided aluminum, which can then undergo thermite-type reactions with compounds (or solvents) containing combined oxygen or halogen.

- All apparatus and reactants should be perfectly dry, and reaction should be run rigorously under nitrogen, with the reaction temperature below 60 °C at all times.
- Order of addition is important. Always first add the hydride to the solvent in the nitrogenpurged apparatus, before the addition of other reactants.
- The hydride should never be allowed to form a crust above the level of the liquid or to settle to the bottom, so efficient and gentle stirring is absolutely essential.
- To prevent local overheating of the reaction vessel, heating mantles should never be used; always used an oil bath as heat source.
- After reduction has been effected, destroy excess LAH by slow and careful addition of dry ethyl acetate (preferable diluted with inert solvent), again under nitrogen and keeping the temperature below 60 °C. All LAH reactions should be carried out behind suitable protective screens."

- May ignite when ground in mortar.
- Use in dehydrating bis(2-methyoxyethyl)ether has resulted in explosions; other experiments involving boron trifluoride diethyl etherate, dibenzoyl peroxide, 1,2-dimethyoxyethane, ethyl acetate, fluroamides also resulted in explosions. Vigorous reactions with pyridine and tetrahydrofuran have also been reported.

DIBAL-H, sodium/potassium borohydride, and sodium cyanoborohydride should be handled as indicated above for LAH.

Additionally – avoid exposing sodium cyanoborohydride to acidic media, as it will release highly toxic hydrogen cyanide gas.

NOTE

Any deviation from this SOP requires approval from PI.

Documentation of Training (signature of all users is required)

- Prior to conducting any work with pyrophoric reagents, designated personnel must provide training to his/her laboratory personnel specific to the hazards involved in working with this substance, work area decontamination, and emergency procedures.
- The Principal Investigator must provide his/her laboratory personnel with a copy of this SOP and a copy of the SDS provided by the manufacturer.
- The Principal Investigator must ensure that his/her laboratory personnel have attended appropriate laboratory safety training or refresher training within the last one year.

I have read and understand the content of this SOP:

Name	Signature	Date

APPENDIX:

Strong Reducing Agents Used in Lab

????

Appendix Y: Water Reactive Chemicals SOP

Standard Operating Procedure

Water Reactive Chemicals

Department:	????
Date SOP written:	????
Date SOP approved by PI/lab supervisor:	????
Principal Investigator:	????
Internal Lab Safety Coordinator/Manager:	????
Lab Phone:	????
Office Phone:	????
Emergency Contact:	????
Location(s) covered by this SOP:	????

Type of SOP:
□ Process □ Hazardous Chemical X Hazardous Class

Purpose

This is a chemical class SOP. Some uses of the chemicals in this class require specific SOPs. Chemical-specific SDSs and all relevant SOPs must be reviewed prior to use of any chemical in this class.

A list of the water reactive chemicals used in this lab is shown in the Appendix at the end of this document.

Physical & Chemical Properties/Definition of Chemical Group

Water reactive chemicals are compounds that react vigorously with water or moist air. Common sensitive chemicals, such as metal hydrides, react with water exothermally (producing heat) and give off flammable hydrogen gas, which may ignite or combine explosively with oxygen found in the atmosphere.

Common groups: Grignard reagents (RMgX); Alkali metals (Li, Na, K); Alkali metal amides; Alkali metal hydrides (Lithium aluminum hydride); Metal alkyls (Lithium and aluminum alkyls); Chlorosilanes; Halides of nonmetals (BCl₃, BF₃, PCl₃, PCl₅, SiCl₄, S₂Cl₂); Inorganic acid halides (POCl₃, SOCl₂, SO₂Cl₂); Anhydrous metal halides (AlCl₃, AlBr₃, TiCl₄, ZrCl₄, SnCl₄); Organic acid halides and anhydrides of low molecular weight.

NOTE: Water reactive material may also present additional hazards such as corrosivity or toxicity. These materials may also have pyrophoric properties.

Potential Hazards/Toxicity

Physical Hazards

When moisture reactive compounds come into contact with water (deliberately or accidentally), an exothermic reaction, generating heat and in some cases a gas, may occur. Violent reactions may occur with even a limited amount of water with some classes of compounds: [alkali and alkaline-earth metals (potassium, magnesium, lithium, calcium, etc.), silicon halides (trichlorosilane, ethyldichlorosilane, methyldichlorosilane), organometallics (lithium alkyls, diethylzinc, dimethylzinc) and metal hydrides (aluminum hydride, calcium hydride, lithium hydride, sodium hydride, etc.)].

The risks associated with a specific chemical depend on its reactivity and the nature of the gaseous product (flammable, toxic, or both). The mutual production of flammable gas and heat can lead to spontaneous ignition or explosion. Typical gases produced are: H_2 , CH_4 , CO, CO_2 , H_2S , NH_3 , HCN, HF, HCl, HI, SO_2 , SO_3 , and oxides of nitrogen (NO, NO₂). Prior to working with any water reactive chemicals, you must identify which gas may be formed and learn the risks associated with this gas.

The reaction rate of solid material (and therefore heat and gas generation) depends, in large part, on the material's surface area. Therefore smaller particle size increases the hazards associated with these materials.

Health Hazards

Some compounds under this category are toxic and may be dissolved in a flammable solvent. Other common hazards include corrosivity and peroxide formation. They may also cause damage to liver, kidneys, mucus membranes and the central nervous system.

Personal Protective Equipment (PPE)

Respiratory protection

NOTE: Lab personnel intending to use/wear a respirator mask must be trained and fit-tested by EH&S. This is a regulatory requirement.

Respirators should be used only under any of the following circumstances:

- As a last line of defense (i.e., after engineering and administrative controls have been exhausted).
- When Permissible Exposure Limit (PEL) has been exceeded or when there is a possibility that PEL will be exceeded.
- Regulations require the use of a respirator.
- An employer requires the use of a respirator.
- There is potential for harmful exposure due to an atmospheric contaminant (in the absence of PEL)
- As PPE in the event of a chemical spill clean-up process

Hand Protection

Always handle water reactive chemicals with gloves.

NOTE: Nitrile gloves are generally recommended; however, consult with your preferred glove manufacturer to ensure that the gloves you plan on using are compatible with specific chemicals.

Refer to glove selection chart from the links below: <u>http://www.ansellpro.com/download/Ansell_8thEditionChemicalResistanceGuide.pdf</u> OR <u>http://www.allsafetyproducts.biz/page/74172</u> OR <u>http://www.showabestglove.com/site/default.aspx</u> OR http://www.mapaglove.com/

Gloves must be inspected prior to use. Use proper glove removal technique (without touching glove's outer surface) to avoid skin contact with this product. Dispose of contaminated gloves after use in accordance with applicable laws and good laboratory practices. Wash and dry hands.

Eye Protection

ANSI approved tight-fitting safety glasses with side shields. Goggles are recommended. Prescription eyeglasses (without side slides) are not adequate protection. Use face shield (8-inch minimum) when appropriate (not protected by fume hood sash for example). Use equipment for eye protection tested and approved under appropriate government standards such as NIOSH (US) or EN 166(EU) or ANSI Z87.1.

Skin and Body Protection

Flame resistant lab coat preferably made of antistatic material, long pants, and closed-toe shoes.

Hygiene Measures

Avoid contact with skin, eyes and clothing. Wash hands before breaks and immediately after handling the product.

Engineering Controls

- Many water sensitive compounds liberate hydrogen when in contact with moisture. A chemical fume hood with exhaust ventilation is required when working with this class of compounds to prevent build up of toxic and flammable gases. The hood sash should be down and serve as a safety shield.
- Water reactive chemicals should be used under water-free conditions (oven- or flamed dried glassware, inert atmosphere).
- Use fresh, dry solvents.
- Keep the material under an inert atmosphere (e.g. nitrogen or argon) when not in use.
- A glove box is available for use when working with particularly reactive chemicals (inert atmosphere).
- Know where your safety equipment is located (i.e., fire extinguisher, eye wash/safety shower, and first aid kit).
- Have the appropriate fire extinguisher available and a small beaker of dry sand in case of small fires. Do not use water in an attempt to extinguish a reactive material fire as it may enhance combustion. The recommended fire extinguisher is a standard dry powder (ABC) type. Class D extinguishers are recommended for combustible solid metal fires (i.e., sodium, potassium, LAH).

First Aid Procedures

If inhaled

Move person into fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Seek medical aid immediately.

In case of skin contact

Wash skin with soap and water for at least 15 minutes while removing contaminated clothing and shoes.

In case of eye contact

Flush eyes with plenty of water for at least 15 minutes. Consult a physician.

If swallowed

Never give anything by mouth to an unconscious person. Ingestion is not considered a potential route of exposure. If suspected that a large amount is swallowed, seek medical attention immediately.

Working Alone

Certain extremely hazardous operations should not be performed if the PI or Lab Safety Contact(s) are not present. Never work alone with extremely hazardous materials/operations.

Precautions for safe handling: Avoid contact with skin, eyes, and clothing. Avoid inhalation. Avoid heat, flames, sparks, and other sources of ignition. Avoid shock or friction. Protect from physical damage.

Conditions for safe storage: Keep container tightly closed in a cool, dry, and well-ventilated area. If possible, store water reactive chemicals in a desiccator.

Spill and Accident Procedure

Spill – Assess the extent of danger. Help contaminated or injured persons. Turn off all sources of ignition. Ventilate potentially explosive atmospheres. Do not put water or flammable materials on spill (i.e., paper towels). For solid water reactive chemical spills, cover with soda ash (sodium carbonate) and shovel into a dry metal container and cover again with soda ash. Dispose of promptly through EH&S. Small containable spills may be quenched with an alcohol (methanol or ethanol) before addition of water to quench remaining reagent. Avoid putting wet chemicals into a covered container as gas evolution may occur. Do not attempt to handle a large spill. Evacuate the area immediately (you and other researchers within the laboratory) and call for assistance (911, EH&S, and your supervisor). Remain on the scene but at a safe distance to direct response personnel when they arrive.

Chemical Spill on Body or Clothes – Remove contaminated clothing and rinse body thoroughly in emergency shower for at least 15 minutes. Seek medical attention. *Notify supervisor and EH&S immediately.*

Chemical Splash Into Eyes – Immediately rinse eyeball and inner surface of eyelid with water from the emergency eyewash station for 15 minutes by forcibly holding the eye open. Seek medical attention. *Notify supervisor and EH&S immediately.*

Article XVI. Medical Emergency Dial 911

Life Threatening Emergency, After Hours, Weekends And Holidays – Dial **911** or go to the nearest emergency room.) <u>Note</u>: All serious injuries <u>must</u> be reported to EH&S within 8 hours.

Non-Life Threatening Emergency – Go to the Occupational Health Facility (OHF). After hours, go to the nearest emergency room. <u>Note</u>: All serious injuries <u>must</u> be reported to EH&S within 8 hours.

Needle stick/puncture exposure (as applicable to chemical handling procedure) – Wash the affected area with antiseptic soap and warm water for 15 minutes. For mucous membrane <u>exposure</u>, flush the affected area for 15 minutes using an eyewash station. After hours, go to the nearest emergency room. <u>Note</u>: All needle stick/puncture exposures <u>must</u> be reported to EH&S within 8 hours.

Decontamination/Waste Disposal Procedure

As a general reminder, be vigilant not to discard PPE having adhered reagent into the waste receptacle; this may lead to accumulation of hydrogen gas or ignition of combustible materials.

General hazardous waste disposal guidelines:

Label Waste

• Affix an appropriate hazardous waste tag on all waste containers using the Online Tag Program <u>http://otp.ucop.edu/</u> as soon as the first drop of waste is added to the container.

Store Waste

- Store hazardous waste in closed containers, in secondary containment and in a designated location.
- Double-bag dry waste using transparent bags.

• Waste must be under the control of the person generating & disposing of it.

Dispose of Waste

- Dispose of regularly generated chemical waste within 90 days.
- Call EH&S for questions.
- Empty Containers.
 - Dispose as hazardous waste if it once held extremely hazardous waste (irrespective of the container size.)
 - Consult waste pick-up schedule.

Prepare for transport to pick-up location.

- Check on-line waste tag.
- Write date of pick-up on the waste tag.
- Use secondary containment.

Safety Data Sheet (SDS) Location

Online SDS can be found online at <u>http://ucmsds.com</u>

Lab-Specific Procedures

Lab-specific procedures for this class of chemicals include storing, dispensing, use in chemical reactions, use in processes (e.g., distillation, rotary evaporation, or chromatography), and disposal. Appropriate personal protective equipment and engineering controls are to be used.

• Lithium aluminum hydride (Example)

From "Hazards in the Chemical Laboratory, 4th Edition," Edited by L. Bretherick. London, The Royal Society of Chemistry, 1986, p79.

"Warning on the use of aluminum lithium hydride (LAH): Following the investigation of a laboratory explosion, Dr. M. L H. Green of the University of Oxford has warned that the following precautions are essential for the safe use of lithium aluminum hydride (LAH). The measures are to prevent overheating of the hydride and dissociation to finely divided aluminum, which can then undergo thermite-type reactions with compounds (or solvents) containing combined oxygen or halogen.

- 1. All apparatus and reactants should be perfectly dry, and reactions should be run under dry nitrogen gas, with the reaction temperature below 60° C at all times.
- 2. Order of addition is important. Always add the hydride first to the solvent in a nitrogen-purged apparatus before adding the other reactant(s).
- 3. The hydride should never be allowed to form a crust above the level of the liquid or to settle to the bottom, so efficient and gentle stirring is absolutely essential.
- 4. To prevent local overheating of the reaction vessel, heating mantles should never be used; always used an oil bath as heat source.
- 5. After a reduction reaction has completed, destroy excess LAH by slow and careful addition of dry ethyl acetate (preferably diluted with an inert solvent), maintaining a nitrogen atmosphere and keeping the temperature below 60° C. All LAH reactions should be carried out behind a closed fume hood sash or suitable protective screen(s).
- 6. May ignite when ground in mortar.

7. Use of anhydrous bis(2-methyoxyethyl) ether has resulted in explosions; other experiments involving boron trifluoride diethyl etherate, dibenzoyl peroxide, 1,2-dimethyoxyethane, ethyl acetate, and fluoroamides have also resulted in explosions. Vigorous reactions with pyridine and tetrahydrofuran have also been reported.

Alkali and alkaline earth metals (such as sodium, potassium, lithium magnesium, calcium, powdered aluminum) should be stored and handled so they cannot contact carbon dioxide, carbon tetrachloride and other chlorinated hydrocarbons, water and water or CO_2 containing fire extinguishers.

Besides water, other reagents may be incompatible with water-reactive compounds. Below is a small list of incompatibles for certain reagents (excerpted from "Hazards in the Chemical Laboratory, 4th Edition," Edited by L. Bretherick. London, The Royal Society of Chemistry, 1986).

- Aluminum hydride: May explode spontaneously at ambient temperatures; violent decomposition in certain methyl ethers in presence of carbon dioxide; forms explosive complexes with tetrazoles.
- Aluminum metal: Violent or explosive reaction with numerous oxidants, butanol, halocarbons, halogens, HCI, mercury salts, silver chloride.
- **Calcium:** Pyrophoric when finely divided. Reacts explosively with PbCl₂, P₂O₂, S, N₂O₄.
- **Calcium carbide:** Vigorous reaction with boiling methanol; forms high sensitive explosives with silver nitrate solutions; explosive with sodium peroxide solutions.
- **Cerium:** Reaction with zinc is explosively violent.
- **Diethylzinc:** Pyrophoric in air; react violently with water, violent reaction with diiodomethane/alkene mixtures, methanol, halogens, AsCl₃, PCl₃, SO₂, nitro compounds.
- **Dimethylzinc:** Ignites in air and explodes in oxygen.
- Lithium: Finely divided metal may ignite in air; will burn in nitrogen or carbon dioxide and is difficult to extinguish once alight; reacts violently with BrF₅ and explosively with diazomethane; mixtures with halocarbons will explode on impact; ignites on contact with nitric acid or sulfur. Powdered Li may explode with bromobenzene.
- Lithium hydride: ignites in warm air; mixtures with liquid oxygen are detonatable explosives.
- **Magnesium:** As a fine powder dispersed in air, it is a serious explosion hazard; reaction with beryllium fluoride is violent; powdered metal may react or explode with contact with chloromethane, chloroform, carbon tetrachloride. Ignites if finely divided on heating in iodine vapor; reacts vigorously with certain cyanides, metal oxides, metal oxide salts, methanol. Mixtures with methanol and water are detonatable.
- **Phosphorus pentasulfide (P₄S₁₀):** ignites by friction, sparks or flames; it heats and may ignite with limited amounts of water.
- **Potassium:** Explosions have occurred when old, heavily encrusted potassium metal has been cut with a knife. Such old stocks should be disposed of uncut. Potassium reacts

readily with CO to form an explosive carbonyl compound. It does not react with air or oxygen in complete absence of moisture, but in its presence oxidation becomes fast, and melting and ignition takes place. Prolonged but restricted access to air results in the formation of yellow superoxide coatings on top of the monoxide. Percussion or dry cutting of the metal brings traces of residual oil into contact with the superoxide and a very violent explosion occurs. Reacts to form shock sensitive compounds with contact with halocarbons; ignites in fluorine and chlorine; explodes or reacts violently with bromine, HI, mercury, metal halides and oxides, non-metal halides and oxides, oxidants, sulfuric acid.

- Sodium: Dispersions of sodium in volatile solvents become pyrophoric when solvent evaporates; can react dangerously with chloroform/methanol, diazomethane, DMF, fluorinated compounds, halocarbons, halogens, mercury, metal halides and oxides, nonmetal halides ad oxides, oxidants, bromobenzene, SnO₂, POCl₃, and sulfides. Mixtures with SO₂F₂, SiCl₄, CS₂, alkyl oxalates, or aromatic nitro compounds are shock sensitive.
- **Sodium amide:** Reacts vigorously with moisture and protonic solvents: may form explosive peroxides upon long term storage or exposure to air.
- **Sodium hydride:** Reacts vigorously with acetylene, DMSO, sulfur, SO₂; exotherm with DMF sets in at 40° C; dry powder ignites in air.
- **Zinc:** Forms pyrophoric compounds with halocarbons. Reacts violently with MnCl₂, KO₂, TiO₂, ZnO₂, sulfur, potassium chlorate, and ammonium nitrate.

NOTE

Any deviation from this SOP requires approval from PI.

Documentation of Training (signature of all users is required)

- Prior to conducting any work with water reactive reagents, designated personnel must provide training to his/her laboratory personnel specific to the hazards involved in working with this substance, work area decontamination, and emergency procedures.
- The Principal Investigator must provide his/her laboratory personnel with a copy of this SOP and a copy of the SDS provided by the manufacturer.
- The Principal Investigator must ensure that his/her laboratory personnel have attended appropriate laboratory safety training or refresher training within the last one year.

I have read and understand the content of this SOP:

Name	Signature	Date

APPENDIX:

Water Reactive Chemicals Used in Lab

1	
Aluminum alkyl halides	
Aluminum alkyl hydrides	
Aluminum alkyls	
Aluminum borohydride, or Aluminum borohydride in device	S
Aluminum Carbide	
Aluminum ferrosilicon powder	
Aluminum hydride	
Aluminum phosphide	
Aluminum powder, uncoated	
Aluminum silicon powder, uncoated	
Barium	
Boron trifluroride, dimethyl etherate	
Calcium	
Calcium carbide	
Calcium cyanamide with more than 0.1percent of calcium	carbide
Calcium hydride	
Calcium manganese silicon	
Calcium phosphide	
Calcium silicide	
Cells, containing sodium	
Cerium, turnings or gritty powder	
Cesium or Caesium	
Diethylzinc	
Dimethylzinc	
Ethyldichlorosilane	
Ferrosilicon, with 30 percent or more but less than 90 pe	ercent silicon
Hexyllithium	
Lithium	
Lithium alkyls	
Lithium aluminum hydride	
Lithium aluminum hydride, ethereal	
Lithium borohydride	
Lithium ferrosilicon	
Lithium hydride	
Lithium hydride, fused solid	
Lithium nitride	
Lithium silicon	
Magnesium alkyls	
Magnesium aluminum phosphide	
Magnesium granules, coated, particle size not less than 1	49 microns
Magnesium hydride	
Magnesium phosphide	
Magnesium silicide	
Magnesium, powder or Magnesium alloys, powder	
Maneb or Maneb preparations with not less than 60 perc	ent Manep
Methyl magnesium bromide, in ethyl ether	
Methyldichlorosilane	boruo
Phosphorus pentasulfide, free from yellow or white phosp Potassium	IUIUS
Potassium Potassium borohydride	
-	
Chemical Hygiene Plan V 10	

Chemical Hygiene Plan

Potassium phosphide Potassium-sodium alloys Potassium-metal alloys Rubidium Sodium Sodium aluminum hydride Sodium amide Sodium borohydride Sodium hydride Sodium phosphide Starmic phosphide Strontium phosphide Trichlorosilane Zinc ashes Zinc phosphide Zinc powder or Zinc dust

Appendix Z: Glossary

ACGIH - The American Conference of Governmental Industrial Hygienists is a voluntary membership organization of professional industrial hygiene personnel in governmental or educational institutions. The ACGIH develops and publishes recommended occupational exposure limits each year called Threshold Limit Values (TLVs) for hundreds of chemicals, physical agents, and biological exposure indices.

ACTION LEVEL - A concentration designated in Title 8, California Code of Regulations for a specific substance, calculated as an eight (8)-hour time weighted average, which initiates certain required activities such as exposure monitoring and medical surveillance.

AEROSOL - Liquid droplets or solid particles dispersed in air that are of fine enough size (less than 100 micrometers) to remain dispersed for a period of time.

ASPHYXIANT - A chemical (gas or vapor) that can cause death or unconsciousness by suffocation. Simple asphyxiants, such as nitrogen, either use up or displace oxygen in the air. They become especially dangerous in confined or enclosed spaces. Chemical asphyxiants, such as carbon monoxide and hydrogen sulfide, interfere with the body's ability to absorb or transport oxygen to the tissues.

"C" OR CEILING - A description usually seen in connection with a published exposure limit. It refers to the concentration that should not be exceeded, even for an instant. It may be written as TLV-C or Threshold Limit Value - Ceiling. (See also Threshold Limit Value).

CARCINOGEN - A cancer-producing substance or physical agent in animals or humans. A chemical is considered a carcinogen or potential carcinogen if it is so identified in any of the following:

- National Toxicology Program, "Annual Report of Carcinogens" (latest edition)
- International Agency for Research on Cancer, "Monographs" (latest edition)
- OSHA, 29 CFR 1910, Subpart Z, Toxic and Hazardous Substances

CHEMICAL HYGIENE OFFICER - An employee who is designated by the employer and who is qualified by training or experience to provide technical guidance in the development and implementation of the provisions of the Chemical Hygiene Plan.

CHEMICAL HYGIENE PLAN - A written program developed and implemented by the employer which sets forth procedures, equipment, personal protective equipment, and work practices that (1) are capable of protecting employees from the health hazards presented by hazardous chemicals used in that particular workplace and (2) meets the requirements of OSHA regulation 29 CFR 1910.1450.

COMBUSTIBLE LIQUID - Any liquid having a flashpoint at or above 100°F (37.8°C) but below 200°F (93.3°C) except any mixture having components with flashpoints of 200°F or higher, the total volume of which make up 99% or more of the total volume of the mixture.

COMPRESSED GAS - A gas or mixture of gases having, in a container, an absolute pressure exceeding 40 psi at 70oF (21.1°C), or; a gas or mixture of gases having, in a container, an absolute

pressure exceeding 104 psi at 130°F (54.4°C) regardless of the pressure at 70oF (21.1°C), or; a liquid having a vapor pressure exceeding 40 psi at 100°F (37.8°C) as determined by ASTM D-323-72.

CORROSIVE - A substance that, according to the DOT, causes visible destruction or permanent changes in human skin tissue at the site of contact or is highly corrosive to steel.

DESIGNATED AREA - An area which has been established and posted with signage for work involving hazards (e.g., "select carcinogens," reproductive toxins, or substances which have a high degree of acute toxicity). A designated area may be the entire laboratory, an area of a laboratory, or a device such as a laboratory hood.

EMERGENCY - Any potential occurrence, such as, but not limited to, equipment failure, rupture of containers, or failure of control equipment which could result in an uncontrolled release of a hazardous chemical into the workplace.

EXPLOSIVE - A chemical that causes a sudden, almost instantaneous release of pressure, gas, and heat when subjected to a sudden shock, pressure, or high temperature.

FLAMMABLE - A chemical that falls into one of the following categories:

- 1. Flammable aerosol an aerosol that, when tested by the method described in 16 CFR 1500.45, yields a flame projection exceeding 18 inches at full valve opening, or a flashback (a flame extending back to the valve) at any degree of valve opening;
- 2. Flammable gas a gas that, at ambient temperature and pressure, forms a flammable mixture with air at a concentration of 13% by volume or less; or a gas that, at ambient temperature and pressure, forms a range of flammable mixtures with air wider than 12% by volume, regardless of the lower limit;
- 3. Flammable liquid any liquid having a flashpoint below 100°F (37.8°C), except any mixture having components with flashpoints of 100°F (37.8°C) or higher, the total of which make up 99% or more of the total volume of the mixture; or
- 4. Flammable solid a solid, other than a blasting agent or explosive as defined in1910.109(a), that is liable to cause fire through friction, absorption of moisture, spontaneous chemical change, or retained heat from manufacturing or processing, or which can be ignited readily and, when ignited, burns so vigorously and persistently as to create a serious hazard. A chemical shall be considered to be a flammable solid if, when tested by the method described in 16 CFR 1500.44, it ignites and burns with a self-sustained flame at a greater than one-tenth of an inch per second along its major axis.

FLASHPOINT - The minimum temperature at which a liquid gives off a vapor in sufficient concentration to ignite in the presence of an ignition source or when tested as follows:

- Tagliabue Closed Tester (See American National Standard Method of Test for Flashpoint by Tag Closed Tested, Z11.24-1979 (ASTM D-56-79) for liquids with a viscosity of less than 45 Saybolt Universal Seconds (SUS) at 100oF (37.8°C) or that contain suspended solids and do not have a tendency to form a surface film under test;
- Pensky-Martens Closed Tester (See American National Standard Method of Test for Flashpoint by Pensky-Martens Closed Tester, Z11.7-1979 (ASTM D-73-79) for liquids with a viscosity equal to or greater than 45 SUS at 100oF (37.8°C), or that contain suspended solids, or that have a tendency to form a surface film under test; or,
- 3. Setaflash Closed Tester (See American National Standard Method of Test for Flashpoint of Setaflash Closed Tester (ASTM D-3278-78)). Organic peroxides, which undergo auto

accelerating thermal decomposition, are excluded from any flashpoint determination methods specified above.

GENERAL VENTILATION - Also known as general exhaust ventilation, this is a system of ventilation consisting of either natural or mechanically induced fresh air movements to mix with and dilute contaminants in the workroom air. This is not the recommended type of ventilation to control contaminants that are highly toxic, when there may be corrosion problems from the contaminant, when the worker is close to where the contaminant is being generated, and where fire or explosion hazards are generated close to sources of ignition. (See Local Exhaust Ventilation)

HAZARD ASSESSMENT - A formal procedure undertaken by the supervisor in which occupational hazards for all employees are described per procedure or task, and by affected body part(s) or organ(s), and which is documented and posted in the workplace with all personal protective equipment requirements.

HAZARD WARNING - Any words, pictures, symbols or combination thereof appearing on a label or other appropriate form of warning which convey the hazards of the chemical(s) in the container(s).

HAZARDOUS MATERIAL - Any material which is a potential/actual physical or health hazard to humans.

HAZARDOUS MATERIAL (DOT) - A substance or material capable of posing an unreasonable risk to health, safety, and property when transported including, but not limited to, compressed gas, combustible liquid, corrosive material, cryogenic liquid, flammable solid, irritating material, material poisonous by inhalation, magnetic material, organic peroxide, oxidizer, poisonous material, pyrophoric liquid, radioactive material, spontaneously combustible material, an water-reactive material.

HAZARDOUS CHEMICAL - A chemical for which there is statistically significant evidence based on at least one study conducted in accordance with established scientific principles that acute or chronic health effects may occur in exposed employees. The term "health hazard" includes chemicals which are carcinogens, toxic or highly toxic agents, reproductive toxins, irritants, corrosives, sensitizers, hepatotoxins, nephrotoxins, neurotoxins, agents which act on the hematopoietic system, and agents which damage the lungs, skin, eyes or mucous membranes. A chemical is also considered hazardous if it is listed in any of the following:

- 1. OSHA, 29 CFR 1910, Subpart Z, Toxic and Hazardous Substances;
- 2. "Threshold Limit Values for Chemical Substances and Physical Agents in the Work Environment," ACGIH (latest edition);
- 3. "The Registry of Toxic Effects of Chemical Substances," NIOSH (latest edition); or
- 4. Director's List.

HIGHLY TOXIC - A substance falling within any of the following categories:

- 1. A substance that has a median lethal dose (LD50) of 50 milligrams or less per kilogram of body weight when administered orally to albino rats weighing between 200 and 300 grams each;
- A substance that has a median lethal dose (LD50) of 200 milligrams or less per kilogram of body weight when administered by continuous contact for 24 hours (or less if death occurs within 24 hours) with the bare skin of albino rabbits weighing between two and three kilograms each; or
- 3. A substance that has a median lethal concentration (LC50) in air of 200 parts per million by volume or less of gas or vapor, or 2 milligrams per liter or less of mist, fume, or dust, when

administered by continuous inhalation for one hour (or less if death occurs within one hour) to albino rats weighing between 200 and 300 grams each.

IGNITABLE - A solid, liquid or compressed gas waste that has a flashpoint of less than 140°F. Ignitable material may be regulated by the EPA as a hazardous waste as well.

INCOMPATIBLE - The term applies to two substances to indicate that one material cannot be mixed with the other without the possibility of a dangerous reaction.

IRRITANT - A substance which, by contact in sufficient concentration for a sufficient period of time, will cause an inflammatory response or reaction of the eye, skin, nose or respiratory system. The contact may be a single exposure or multiple exposures. Some primary irritants: chromic acid, nitric acid, sodium hydroxide, calcium chloride, amines, metallic salts, chlorinated hydrocarbons, ketones and alcohols.

LABEL - Any written, printed or graphic material displayed on or affixed to containers of chemicals, both hazardous and non-hazardous.

LABORATORY TYPE HOOD - A device located in a laboratory, enclosed on five sides with a movable sash or fixed partial enclosure on the remaining side; constructed and maintained to draw air from the laboratory and to prevent or minimize the escape of air contaminants into the laboratory; and allows chemical manipulations to be conducted in the enclosure without insertion of any portion of the employee's body other than hands and arms.

LABORATORY USE OF HAZARDOUS CHEMICALS - Handling or use of such chemicals in which all of the following conditions are met:

- 1. Chemical manipulations are carried out on a "laboratory scale";
- 2. Multiple chemical procedures or chemicals are used;
- 3. The procedures involved are not part of a production process nor in any way simulate a production process; and
- 4. 4. "Protective laboratory practices and equipment" are available and in common use to minimize the potential for employee exposure to hazardous chemicals.

LOCAL EXHAUST VENTILATION (Also known as exhaust ventilation) – A ventilation system that captures and removes the contaminants at the point they are being produced before they escape into the workroom air. The system consists of hoods, ductwork, a fan, and possibly an aircleaning device. Advantages of local exhaust ventilation over general ventilation include: it removes the contaminant rather than dilutes it, requires less airflow and, thus, is more economical over the long term; and the system can be used to conserve or reclaim valuable materials; however, the system must be properly designed with the correctly shaped and placed hoods, and correctly sized fans and ductwork.

SAFETY DATA SHEET (SDS) - Written or printed material concerning a hazardous chemical which is prepared in accordance with paragraph (g) of 29 CFR 1910.1200. Formerly known as a Safety Data Sheet (SDS).

MEDICAL CONSULTATION - A consultation which takes place between an employee and a licensed physician for the purpose of determining what medical examinations or procedures, if any, are appropriate in cases where a significant exposure to a hazardous chemical may have taken place.

MIXTURE - Any combination of two or more chemicals if the combination is not, in whole or in part, the result of a chemical reaction.

MUTAGEN - Anything that can cause a change (or mutation) in the genetic material of a living cell.

NFPA - The National Fire Protection Association; a voluntary membership organization whose aims are to promote and improve fire protection and prevention. NFPA has published 16 volumes of codes known as the National Fire Codes. Within these codes is Standard No. 705, "Identification of the Fire Hazards of Materials". This is a system that rates the hazard of a material during a fire. These hazards are divided into health, flammability, and reactivity hazards and appear in a well-known diamond system using from zero through four to indicate severity of the hazard. Zero indicates no special hazard and four indicates severe hazard.

NIOSH - The National Institute for Occupational Safety and Health; a federal agency that among its various responsibilities trains occupational health and safety professionals, conducts research on health and safety concerns, and tests and certifies respirators for workplace use.

ODOR THRESHOLD - The minimum concentration of a substance at which a majority of test subjects can detect and identify the substance's characteristic odor.

OXIDIZER - Is a substance that gives up oxygen easily to stimulate combustion of organic material.

PERMISSIBLE EXPOSURE LIMIT (PEL) - An exposure, inhalation or dermal permissible exposure limit specified in 8 CCR 5155. PELs may be either a time-weighted average (TWA) exposure limit (8-hour), a 15-minute short-term limit (STEL), or a ceiling (C).

PERSONAL PROTECTIVE EQUIPMENT - Any devices or clothing worn by the worker to protect against hazards in the environment. Examples are respirators, gloves, and chemical splash goggles.

PHYSICAL HAZARD - A chemical for which there is scientifically valid evidence that it is a combustible liquid, a compressed gas, explosive, flammable, an organic peroxide, an oxidizer, pyrophoric, unstable (reactive), or water-reactive.

PYROPHORIC - A chemical that will spontaneously ignite in the air at a temperature of 130oF (54.4oC) or below.

REACTIVITY - A substance's susceptibility to undergoing a chemical reaction or change that may result in dangerous side effects, such as explosion, burning, and corrosive or toxic emissions. The conditions that cause the reaction, such as heat, other chemicals, and dropping, will usually be specified as "Conditions to Avoid" when a chemical's reactivity is discussed on an SDS.

REPRODUCTIVE TOXINS - Chemicals which affect the reproductive capabilities including chromosomal damage (mutations) and effects on fetuses (teratogenesis).

RESPIRATOR - A device which is designed to protect the wearer from inhaling harmful contaminants.

RESPIRATORY HAZARD - A particular concentration of an airborne contaminant that, when it enters the body by way of the respiratory system or by being breathed into the lungs, results in some body function impairment.

SELECT CARCINOGENS - Any substance which meets one of the following:

1. It is regulated by OSHA as a carcinogen; or

2. It is listed under the category, "known to be carcinogens," in the Annual Report on Carcinogens published by the National Toxicology Program (NTP) (latest edition);or

3. It is listed under Group 1 ("carcinogen to humans") by the International Agency for Research on Cancer Monographs (IARC)(latest editions); or

4. It is listed in either Group 2A or 2B by IARC or under the category, "reasonably anticipated to be carcinogens" by NTP.

SENSITIZER - A substance that may cause no reaction in a person during initial exposures, but afterwards, further exposures will cause an allergic response to the substance.

SHORT-TERM EXPOSURE LIMIT - Represented as STEL or TLV-STEL, this is the maximum concentration to which workers can be exposed for a short period of time (15 minutes) for only four times throughout the day with at least one hour between exposures. Also the daily TLV-TWA must not be exceeded.

SOLVENT - A substance, commonly water, but in industry often an organic compound, which dissolves another substance.

THRESHOLD LIMIT VALUE (TLV) - Airborne concentration of substances devised by the ACGIH that represents conditions under which it is believed that nearly all workers may be exposed day after day with no adverse effect. TLVs are advisory exposure guidelines, not legal standards, that are based on evidence from industrial experience, animal studies, or human studies when they exist. There are three different types of TLVs: Time-Weighted Average (TLV-TWA), Short-Term Exposure Limit (TLV-STEL), and Ceiling (TLV-C). (See also PEL).

TOXICITY - A relative property of a material to exert a poisonous effect on humans or animals and a description of the effect and the conditions or concentration under which the effect takes place.

VAPOR - The gaseous form of substances which are normally in the liquid or solid state (at normal room temperature and pressure). Vapors evaporate into the air from liquids such as solvents. Solvents with lower boiling points will evaporate faster.