UNIVERSITY OF
SOUTH DAKOTA

Chemical Safety Manual

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Introduction

A safe working and learning environment is an expectation of USD and is provided to all employees, students, and guests at the highest level reasonably possible. The University of South Dakota Chemical Safety Manual is designed as a reference for individual laboratories to provide a safe and productive work and study environment while complying with applicable federal and state rules and best practices. Each laboratory group should supplement this policy when necessary to ensure that the health and safety of workers and students are not compromised.

Radiation Safety is addressed in the University of South Dakota's Radiation Safety Policy for Authorized Workers.

The information is in accordance with guidance found in the National Research Council's Prudent Practices in the Laboratory (National Academy Press, 1995) and the Occupational Safety and Health Administration (OSHA) *Occupational Exposures to Hazardous Chemicals in Laboratories* (29 CFR 1910.1450). The Chemical Safety section outlines the University of South Dakota's Chemical Hygiene Plan.

While this guide is a sufficient starting point, some laboratories may need to supplement this guide with their own workplace specific standard operating procedures (SOPs).

UNIVERSITY OF SOUTH DAKOTA

Responsibility for Laboratory Safety

The Principle Investigator (PI) and/or Laboratory Manager, has primary responsibility for ensuring the safety of students, faculty, staff, visitors, and the environment with respect to their laboratory operations. The Environmental Health and Safety office can provide guidance or information for questions regarding chemical and biological safety. PIs and Laboratory Managers must explain the following to their laboratory personnel.

General safety procedures such as:

- What type of Personal Protective Equipment (PPE) to use
- Any restricted activities (e.g., no food or drink in the lab)
- Safe practices specific to the activities being performed and applicable safety protocol
- What to do in the event of an emergency and how to report emergencies and accidents/injuries
- Location of spill kit/response materials and how to respond to specific chemical spills associated with their work.
- Sink disposal regulations, labeling and management of chemical waste containers

In addition to the training requirements, the PI/Laboratory Manager is also responsible for the following:

- Monitor operations for safety, advising laboratory students and staff on safety matters, and serve as a focus for safety concerns of the laboratory staff
- Investigate accidents and near misses and report them to the appropriate supervisors. The Environmental Health & Safety office is available to assist in any incident if help is desired
- Monitor storage, labeling, and use of hazardous materials
- Maintain a complete written current inventory of all chemicals, gases, biological, lasers, radioactive, and other hazardous materials in their areas of supervision

The Director, Environmental Health and Safety (EHS), is responsible for implementing the University's chemical and biological safety programs.

The Director, EHS, will:

- monitor compliance with safety practices and procedures regarding chemical and biohazardous materials
- work with faculty and staff to develop and implement appropriate safety practices and policies
- ensure that safety audits are performed periodically and that results are reported to the responsible parties
- provide consultation to investigators on matters relating to laboratory safety, appropriate handling and containment of hazardous materials, decontamination and disposal of hazardous wastes
- serve as liaison between the University and outside regulatory agencies.
- Serve as Chemical Hygiene Officer

General Laboratory Practices

All chemicals are, to some degree, poisonous to the human body. Here we will review general laboratory safety practices, procedures and equipment which all researchers and students must know, understand and apply to their laboratory work.

General Safety Procedures

1. Know the materials you are working with (e.g. chemical, biological, radioactive)
   a. Refer to and follow your laboratory protocols.
   b. Review the Safety Data Sheets (SDS) for chemicals. These should be available and easily accessible in each laboratory either as hardcopy or electronic.
   c. Consider the toxicity of materials, the health and safety hazards of each procedure, the knowledge and experience of laboratory personnel and the safety equipment that is available. If you are uncertain about any aspect of handling the material, talk to your PI or lab supervisor before using.
2. Know the location of safety equipment and emergency procedures in your area.
3. Always wear appropriate clothing (e.g. pants, shirts, shoes) and personal protective equipment (e.g. safety glasses, lab coats, gloves) when working in the laboratory. Open-toed shoes and sandals are unacceptable footwear; shorts and skirts are not recommended. These items do not protect the feet and lower legs from spills or broken glass. Remove personal protective clothing and wash hands before leaving the laboratory.
4. Avoid working alone in the laboratory when hazardous operations are conducted.
5. Use a properly operating fume hood when working with hazardous fuming chemicals.
6. Mechanical pipetting devices should be used. Mouth pipetting is unacceptable.
7. Do not eat, drink, prepare food or apply cosmetics in the laboratory.
8. Keep work areas clean and uncluttered at all times.
9. Do not leave experiments unattended, especially experiments using a heat source such as water baths, hot plates, etc.
10. Unauthorized individuals are prohibited from entering the laboratory. The laboratory manager should approve all visitors, and visitors / guests should not be left unattended.
11. Persons under 18 years of age should not be involved in procedures involving hazardous chemicals.
12. Volunteer workers in any research laboratory must be registered with Human Resources.
13. Non-laboratory and non-assistance animals are not allowed in campus buildings.

Security

Laboratory security is an integral part of an effective safety program. To provide a safe working environment, follow the steps outlined below.

1. Keep laboratory doors locked when the lab is unoccupied.
2. Keep an accurate inventory of chemicals.

Laboratory Safety Equipment

All personnel within a laboratory should know the location of all safety equipment outlined below.

1. **Safety Showers**: Safety showers are used in an emergency to flush and dilute chemicals that laboratory personnel or their clothing have been contaminated with. The most effective use of the safety shower is to turn on the shower and remove contaminated clothing while standing under the shower. The Safety Shower can also be used to extinguish a clothing fire.
2. **Eye and Face Washes:** For chemical splashes of the eye and face, immediately flush with a large quantity of water for 15 minutes. The path of travel from the hazard to the equipment should be free of obstructions.
3. **Fire Extinguishers**: Fire extinguishers are placed in every laboratory.
4. **First Aid Kits**: First aid kits should be available in each laboratory. The responsibility for first aid kits lies with the laboratory manager or PI. First aid kits should NOT contain oral medicines (e.g., aspirin), topical creams, liquids or ointments that can cause further discomfort and/or hinder medical treatment.
5. **Laboratory Safety Information**: Safety Data Sheets (SDS's), emergency procedures, safety policies, and other references should be readily available for all laboratory personnel. The laboratory should designate a single location for this information.
6. **Door Postings and Other Signs**: Hazard and emergency information signs may be posted on the laboratory door or wall facing the corridor. These signs are used by *emergency response personnel* to identify hazards within the laboratory. It is needed to provide a point-of-contact in the event of an accident, chemical spill, fire, or personal injury.
7. **Sharp Containers and Broken Glass Boxes**: Sharps containers are used for the disposal of hypodermic needles and syringes, razor blades, and other sharp items that could potentially puncture skin. When ¾ full, sharps containers should be sealed and processed according to local unit procedures. While sharps containers may be used for contaminated broken glass, never "rebreak" glass to facilitate placement in a sharps container. If broken glass has been contaminated with a biological agent the glass should be disposed of in a sharps container. If the biologically contaminated glass will not fit in the sharps container, a second container must be used that will be processed by the same method as a sharps container. For any broken glass that is not biologically contaminated, it may be disposed of in a broken glass box and disposed of in a dumpster.

Personal Protective Equipment (PPE)

Personal protective equipment (e.g., safety glasses, goggles, gloves, lab coat, etc.) help protect laboratory personnel from both physical and health effects of a chemical. This PPE must be available for laboratory personnel who are working with hazardous materials. Laboratories must also provide personal protective equipment for visitors. In areas where eye protection is needed, a sign must be posted in a prominent location.

Eye and face protection must be worn in the laboratory when there is a potential for eye contact with hazardous chemicals or other agents and objects (e.g., UV or laser radiation, biohazardous materials, aerosolized material, flying objects). The type of protection needed depends on the hazard presented by the task. Remember that procedures that may promote aerosolization or volatilization of materials should always be regarded as potentially high risk. As a rule, whenever hazardous laboratory chemicals are used, appropriate eye protection is mandatory. Goggles or over-sized safety glasses should be worn over prescription eyeglasses. Face shields are worn when working with an agent that may adversely affect the skin on the face and/or when standard eye protection is not enough.

Eye, skin, and face protection are required when working with corrosive or reactive chemicals, with glassware under pressure, in combustion and other extreme temperature operations, and whenever there is a possibility of explosion or implosion, no matter how remote the possibility. Special safety glasses and face shields may also be required for work with UV light and laser radiation which is absorbed by the eyes or skin.

Laboratory coats and closed toed shoes should be worn when working in the laboratory. Lab coats should be regularly cleaned. Lab coats, aprons, and gloves should be removed when leaving the laboratory.

Protective gloves should be carefully selected for their material degradation and permeation characteristics so they will provide proper protection.

Protective Clothing outside the Laboratory

Wearing personal protection equipment outside of the laboratory is regarded as poor laboratory practice. If your PPE is contaminated, then the wearing of the contaminated PPE outside of the laboratory increases the risk of spreading the contaminant to other non-research areas. If you are transporting something from one lab to another, follow these guidelines:

- Wearing gloves outside the lab should be minimized, except to move hazardous materials between laboratories. Instead, transport chemicals on a cart, in a clean secondary container, or in a bottle carrier with secure handles.
- For the sake of safety, appearances, and courtesy, do not wear contaminated, stained, or potentially contaminated lab coats and other research clothing and equipment outside of the lab.

Standard Precautions: Removing Gloves Safely

To remove gloves without spreading germs or chemicals, never touch your skin with the outside of either glove. Follow these steps:

1.

- Grasp the palm of one glove near your wrist.
- Carefully pull the glove off.

2.

- Hold the glove in the palm of the still-gloved hand.
- Slip two fingers under the wrist of the remaining glove.

3.

- Pull the glove until it comes off inside out.
- The first glove should end up inside the glove you just took off.
- Dispose of the gloves safely.

4.

- Always wash your hands after removing gloves. Gloves can have holes in them that are too small to be seen.

When to Wear Gloves

Before putting on gloves, wash and dry your hands well. Cover scratches or scrapes with bandages.

- Wear gloves whenever contact is possible with blood, all body fluids, or hazardous chemicals.
- Wear gloves when touching any item or area that may be contaminated.
- Avoid touching uncontaminated items with contaminated gloves.
- Remove gloves right after use. Do not reuse disposable gloves.

Minors in Laboratories

The concern of the University of South Dakota (USD) for laboratory safety extends to all persons visiting USD laboratories. Laboratories are common sources of thermal dangers, compressed gases, electrical hazards, chemical, biological, and radioactive materials, lasers, and sharp objects.

Children under the age of 12

Laboratories must **never** be utilized as a substitute for day care or other childcare options due to the risk presented to a child's developing immune/neurological systems and a child's general inability to recognize hazards. No one under the age of 12 is permitted in USD laboratories. This includes instances when an employee office is inside a laboratory space.

Visitors Ages 12 to 18

Non-USD students between the ages of 12 and 18 who are passing through or touring a laboratory must be under the direct supervision of a USD employee who is trained and knowledgeable of the area's hazards. Persons between the ages of 12 and 18 may be present in laboratories *solely as observers* (unless the person is (a) a USD student who has received the necessary training, or (b) a high school student who is part of an officially sanctioned educational program for high school students or other supervised educational activity that has been approved in writing in advance by the Department Chair or designee.

The University of South Dakota is committed to providing educational opportunities, when they arise, to high school students participating in officially sanctioned educational programs. Principal Investigators are allowed to have high-school students (9th grade and above) perform work in a laboratory. High school students ages 15 and older may handle lower risk chemicals in limited circumstances, with proper safety equipment as necessary, at the discretion of the principal investigator.

Before a high school student may participate in educational activities in a laboratory:

- The student must be sponsored by a faculty member
- The student and his/her parents or guardian must sign the Minor Release and Waiver of Liability Form. The form must be kept on file with the PI's safety records. The signed form must be readily available in an emergency, so that if the student is ill or injured medical personnel may be shown the student's medical treatment consent
- The high school student or minor must be appropriately trained in laboratory safety, and a record of this training must be maintained by the PI.
- High School students and minors must be under direct supervision in the laboratory at all times by a trained and knowledgeable University employee

Safety Data Sheets (SDS)

OSHA requires chemical manufacturers and suppliers to provide Safety Data Sheets (SDS) to communicate the hazards of chemical products. SDSs are designed to provide information needed to protect workers from hazards associated with a chemical. Labs are required to have SDS's for all chemicals in their work space and have them readily available to workers.

Alternatively, the lab may decide to print the SDS's for the chemicals present and maintain a hard-copy library in the lab.

A SDS provides fundamental health and safety information related to a chemical. This information allows you to prepare for potential hazards associated with a chemical and allow to you react to an emergency situation. Workers should review SDSs for chemicals they will be working with if they are unfamiliar with the chemical.

Emergencies and Accidents

The University Police Department responds to most routine emergencies on campus. If there is a life-threatening emergency dial 9-911. This will connect you to the Vermillion 911 operator. Telephones on campus will also display the physical address of the caller. Dialing 911 from a cell phone will not provide the 911 operator with an address. In all emergencies and accidents, the first consideration is your safety and the safety of those around you. For non-emergency assistance on campus call USD Police Department at 605-658-6199

Preparation

Be prepared for an emergency; know the hazards of all compounds/equipment you work with. Assess the risks before using any chemical or biological compound. Where appropriate, post the proper procedures for handling the material and what procedures to follow in the event of a spill or other emergency. Emergency procedures should be posted in a conspicuous location to facilitate emergency responders' assessment.

- For chemical hazards, the SDS should be a primary reference for risk analysis. Risk analysis will include the following criteria:
- Toxicity, reactivity, and flammability of the compound both as an individual agent and in combination with other agents you may be using at the same time
- The amounts involved (smaller is better)
- The expected duration of your exposure to the compound
- Potential routes of entry for the chemical (inhalation, ingestion, injection, skin contact). Remember to include how your handling of the material may increase your risk of exposure.

Chemical Spill:

1. Alert all persons nearby
2. Assess the risk (size of spill)
    a. If you know the material's chemical properties and believe the size and hazard to be small, clean it up being sure to use appropriate PPE. Package and label absorbent/cleaning materials as hazardous waste
    b. For a major spill, one you cannot clean yourself, avoid breathing vapors and turn off ignition sources if the material is flammable. Evacuate the area and close the door to the laboratory. Immediately notify the laboratory manager
    c. If the spill occurs after normal hours and you cannot contact the laboratory manager, contact USD Police Department 605-658-6199 for assistance

Environmental Chemical Releases

If a hazardous material spill gets out to the environment (via floor drain, sink drain, ground, etc.) immediately contact your laboratory manager or USD Police Department. Without endangering yourself, attempt to use absorbent material to contain the spill/release.

1. Extinguish all sources of ignition
2. Isolate all potential environmental outlets (drains, sumps, soil, etc.)
3. Immediately notify the laboratory manager and USD Police Department and wait for them to respond. It is important to record both the chemical compound spilled and the volume.

Fire or Explosion

1. Evacuate the area and close the door
2. Notify occupants nearby
3. Activate the building fire alarm system
4. Evacuate and stay clear of the building but close enough to provide information to emergency responders

Do not attempt to put out a fire unless you are experienced and trained in how to use the fire extinguisher.

Accidents and Injuries

For serious injuries that require medical evacuation, immediately call 9-911 from any campus telephone. All other (minor) injuries should be assessed by a medical care provider and should be reported as soon as possible to the laboratory manager and the Director of EHS or Director of Human Resources.

For potentially toxic chemical exposure, medical personnel should be provided with:

- Identity of chemical or biological SDS
- Condition under which exposures occurred
- Signs and symptoms of exposure

Exposure Monitoring and Medical Treatment

Regular environment or employee exposure monitoring is not warranted or practical in laboratories because the chemicals used are often in well understood procedures, use is for relatively short periods of time and quantities generally small. Good laboratory procedures are carefully designed to ensure minimal exposure. Laboratory workers who suspect that they have been overexposed to a toxic chemical should report to their laboratory manager or the Director of EHS, call 9-911(emergency), or 605-658-6199(USD Police Department for non-emergency).

Medical Examination and Consultation

- Medical examination and consultation is generally not needed for routine laboratory exposures. However, medical examination and/or consultation is recommended in the following situations:
- A worker or visitor develops signs and symptoms of acute exposure
- An event takes place with the likelihood of an individual being exposed
- There are special concerns about exposure to specific chemicals (reproductive toxins, carcinogens, etc.)
- Personnel are engaged in laboratory animal handling and care or are handling human blood, body fluids, or tissues

Training

Faculty members are responsible for ensuring that their employees and students receive proper training. The EHS Department can provide all training if requested to do so.
Training requirements differ depending upon the actual hazardous material and work condition. Safety training should include:

- The hazards of chemical and biological agents in the work area and how to protect against them
- The location of SDS and other hazard information in the laboratory
- How to manage and dispose of waste or unwanted materials
- How to detect the presence or accidental release of a hazardous chemical or biohazard and how to clean up a spill or disinfect a biohazard

Training records will be maintained by the laboratory manager.

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EMERGENCY INFORMATION

Fill out laboratory specific information and post conspicuously.

Information Needed	Response
Lab Location	
Principal Investigator/Laboratory Manager	
After-Hours Contact Information **Names and phone numbers**	
Location Of Chemical Spill Kit	
Location Of Fire Extinguisher	
Location Of Fire Alarm	
Location of Eye Wash Station	
Location of Safety Shower	

USD Environmental Health and Safety

Kevin O'Kelley, Director of Environmental Health & Safety
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Office 605-658-3766
Cell (510) 487-0763

Scott Pottorff, Safety Officer
Email: Scott.pottorff@usd.edu
Office 605-658-6109
Cell (712) 898 –4254

Facilities Management Call Desk: 605-677-6100 (After hours, call USD Police Department)

USD Police Department: 605-658-6199

Fire/Police/Emergency Medical Services Dispatch: 9-911

Chemical Storage Guidelines

Proper chemical storage is a key component in laboratory safety. The following guidelines are taken from *Prudent Practices in the Laboratory* and C*hemical Storage Plan for Laboratories*.

General Rules of Storage:

<u>Do:</u>

< Make certain all chemicals are labeled clearly to identify contents.
< Physically separate incompatible chemicals.
< Segregate by hazard class: Health Hazards (Toxins, Poisons, Carcinogens, etc.), Corrosives, Reactives/Oxidizers, Flammables, and General Storage (e.g. salts and other routine dry chemicals - relatively modest hazards).
< Mark the date on the label when the chemical is received. (Dating containers is especially important for chemicals with a short shelf life like ethyl ether which, because of its explosion hazard, should not be kept for more than 12 months after being opened and must never be kept past its expiration date)
< Keep exits, passageways, areas under benches and desks, and emergency equipment free of stored equipment and materials.

<u>Do not:</u>

< Store chemicals on benches.
< Store chemicals in fume hoods or under sinks.
< Expose to heat or direct sunlight.
< Store hazardous materials above shoulder height of shortest person in lab.

Hazard specific storage rules:

Health Hazards:

< Separate toxins and poisons from other chemicals in a location labeled “Toxins” or “Poisons”.

Corrosives:

< Store large bottles on a low shelf or in a corrosives cabinet.
< Segregate acid oxidizers from organic acids, flammable and combustible materials.
< Segregate acids from bases and active metals.
< Segregate acids from chemicals which can generate toxic gases on contact (e.g. sodium cyanide)
< Segregate perchloric acid from reducing agents and organics.
< Store in chemical resistant trays.

Reactives/Oxidizers:

< Store water-reactive chemicals in a cool and dry place.
< Store oxidizers away from flammables, combustibles, and reducing agents (zinc, alkaline metals, etc.).
< Store peroxide forming chemicals in an airtight container in a cool, dry, dark place. (Peroxide forming chemicals should be disposed of within 12 months of opening, or by expiration date.)
< Shock sensitive and detonatable materials should be stored in a secondary container, large enough to hold entire contents in case of breakage
< Store liquid organic peroxides at the lowest possible temperature consistent with solubility and/or freezing points.

Flammables/Combustibles:

< Store flammable liquids in flammable storage cabinet.
< Do not store flammable liquids in domestic refrigerators or freezers.
< Store away from ignition and heat sources.
< Stay within NFPA rules for volume of flammables: -Maximum for any lab is 120 gallons.
-With flammable safety cabinet - 10 gal/100 sq. ft. unsprinkled or 20 gal/100 sq. ft. of sprinkled area.
-Without flammable safety cabinet - 10 gallons in original container & 25 gallons in 2.5 gallon or smaller safety cans.

Gas Cylinders:

< Strap or chain securely to bench top or wall.
< Cap cylinders not in use.
< Separate incompatibles.
< Segregate empty cylinders from full ones.

Proper chemical storage can prevent many common laboratory accidents. The time and effort required to segregate and store chemicals according to their hazard classes is repaid by increasing the overall safety in any lab.

The following are prohibited from drain disposal:

- Any flammable liquids with a flashpoint less than 140 degrees F – including but not limited to any quantity of gasoline, kerosene, naphtha, benzene, toluene, xylene, fuel oil, ethers, ketones, aldehydes, chlorates, perchlorates, bromates, carbides, hydrides and sulfides.
- Explosive chemicals
- Solutions outside the pH range of 5.5 to 9.5. Labs may neutralize acids and bases to a pH within this range and then drain dispose, provided there are no prohibited items in the solution.
- Halogenated hydrocarbons and aqueous mixtures containing halogenated hydrocarbons
- Insoluble materials
- Mercury Metal
- Aqueous waste with toxic heavy metals (chromium, cadmium, silver, etc.)
- Water reactive materials (including but not limited to aluminum alkyls, barium, lithium, potassium, sodium, sodium borohydride, zinc powder or zinc dust)
- Radioactive materials above a certain activity level (contact EHS for guidance)
- Infectious substances
- Any solids or viscous substances capable of causing obstruction to the flow of sewers, including but not limited to:
    - Grease
    - Particulates greater than ½ inch in any direction
    - Animal products (gut or tissue, paunch manure, bones, hair, hides or fleshing, entrails, whole blood, feathers)
    - Ashes, cinders, sand, spent lime, stone or marble dust, metal, glass, straw, shavings, spent grains
    - Water soluble polymers that could form gels in the sewer system

- Any chemical that either alone or if mixed with other wastes results in the presence of toxic gases, vapors and/or fumes that could be harmful to utilities workers, workers of the Vermillion Wastewater Treatment Facility or create a public nuisance
- Malodorous chemicals such as Mercaptans, hydrogen sulfide, sulfur dioxide, etc.
- Carcinogens, Mutagens or Teratogens, such as Ethidium Bromide
- Pharmaceutical waste (medicines, etc.)

Corrosives (Acids and Bases)

Hazard Properties:

Corrosives can seriously burn body tissue on contact as well as cause dermatitis and eye damage. Exposure to vapors or mists can affect the respiratory tract and mucous membranes.

Corrosives are usually not flammable, but they can react with each other and with other chemicals, causing potential fire and explosion.

Contact with ordinary materials such as paper and wood may generate sufficient heat to ignite. This is especially true for oxidizing acids such as nitric acid and perchloric acid.

Many corrosives may cause delayed injury, particularly bases. The absence of immediate symptoms may prolong exposure and as a result, cause even more severe injuries.

Practices:

Be aware of the nearest eyewash station and emergency shower. If a chemical splash occurs, flush with running water for at least 15 minutes and seek medical attention.

Use chemical splash goggles or other eye protection when working with acids/bases.

Appropriate acid- and base-resistant protective clothing, including aprons, lab coats, and gloves, should also be worn.

When diluting acids or bases with water, always pour the reagent slowly (while mixing) into the water, never the reverse.

Hydrofluoric acid can cause severe chemical burns. Contact EH&S immediately about HF contamination for specific information on a recommended first-aid treatment paste that regular HF users should have on hand.

Whenever acid, base or solvent bottles are carried from the laboratory, the bottles should be placed in buckets which act as secondary protective containers.

Cryogenic Liquids

Cryogenic liquids such as liquid nitrogen, helium, and oxygen are, by definition, extremely cold. Contact between cryogenic liquids and exposed skin can produce a painful burn. A splash of cryogenic liquid to the eye can cause loss of vision. Always wear proper personal protective equipment including a buttoned lab coat, cryogenic apron and long pants or a long skirt, heavy leather gloves (or cryogen handling gloves), safety goggles, and a face shield (when the risk of splash is high) whenever handling cryogenic liquids.

Other Hazards Associated With Cryogenic Liquids

Pressure buildup. Boiling of liquefied gases within a closed system increases pressure. Users must make certain that cryogenic liquids are never contained in a closed system. Cold fingers and similar devices have exploded when either an ice dam is formed within the apparatus or when users create a closed system by shutting off all valves. Users should also tape exposed glass parts to minimize the hazard of flying glass shards in the event of an explosion.

Oxygen enrichment. Liquid nitrogen and liquid helium may fractionally distill air, causing liquid oxygen to collect in the cryogenic container. Liquid oxygen increases the combustibility of many materials, creating potentially explosive conditions. When working with cryogenic liquids in a closed system, be sure to provide a relief valve in case of over-pressurization.

Asphyxiation. If vented into a closed space, a cryogenic liquid will vaporize, displacing oxygen and possibly causing asphyxia. For this reason, never store a container of cryogenic liquid in an enclosed space.

Embrittlement. Do not dispose of cryogenic liquids down the drain! Ordinary materials such as metal or polyvinylchloride (PVC) piping in laboratory sinks may not be able to withstand cryogenic temperatures. Allow cryogenic liquids to evaporate in a fume hood or other well-ventilated areas. Materials exposed to cryogenic temperatures for long periods of time or materials that have undergone periodic warming and freezing must be examined regularly for cracks and warping.

Cryotube Explosions. Cryotubes used to contain samples stored under liquid nitrogen may explode without warning. Tube explosions are caused by liquid nitrogen entering the tube through minute cracks or cap threads and then expanding rapidly as the tube thaws. In addition to wearing proper safety equipment, when thawing cryotubes place the cryotube in a heavy walled container (e.g., a desiccator) or behind a safety shield to protect yourself in the event that the tube shatters.

Flammable and Combustible Liquids

Properties of Flammable & Combustible liquid

Flammable liquid fires are much more volatile than fires fueled by ordinary combustibles such as wood, paper and cloth. Flammable vapors can ignite with explosive force and the resulting fire gives off more than twice as much heat as ordinary combustibles.

Because of these hazards, special precautions are required when storing, handling and using flammable liquids.

Flammable and Combustible Liquids Storage

Flammable liquids shall not be stored in residence halls or in assembly areas.

Flammable and Combustible liquids per control area:

Flammable Liquid Class	Limit
Class 1-A	30 Gallons
Class 1-B	120 Gallons
Class 1-C	120 Gallons
Combination	120 Gallons

Combustible Liquid Class	Limit
Class II	120 Gallons
Class III-A	330 Gallons
Class III-B	13,200 Gallons

These quantities may be increased by 100% if in an approved flammable liquid storage cabinet and may be increased by an additional 100% if in a fully sprinkled building.

Vessels used to store flammable liquids must be clearly marked as to contents and shall comply with the following criteria:

MAXIMUM SIZE

Container – CLASS	1-A	1-B	1-C	II	III
Glass	1 pt	1 qt	1 gal	1 gal	5 gal.
Metal/ Listed Approved Plastic	1 gal	5 gal	5 gal	5 gal	5 gal
Safety Can	2 gal	5 gal	5 gal	5 gal	5 gal
Approved Plastic	0 gal	0 gal	0 gal	0 gal	5 gal
Metal Drum	60 gal	60 gal	60 gal	60 gal	60 gal

Properties and NFPA Classification of Some Common Laboratory Chemicals

Chemical	Flash Point (F)	Boiling Point (F)	NFPA Classification
Acetic Acid, Glacial	103	245	II
Acetone	-4	133	IB
Acetaldehyde	-38	70	IA
Acetonitrile	42	179	IB
Acrylonitrile	32	171	IB
Benzene	12	176	IB
Tert-Butyl Alcohol	52	181	IB
Cyclohexene	<20	181	IB
Dioxane	54	214	IB
Ethyl Acetate	24	171	IB
Ethyl Alcohol	55	173	IB
Ethyl Ether	-49	95	IA
Gasoline	-45	100-400	IB
Hexane	-7	156	IB
Isopropanol	53	183	IB
Methanol	52	174	IB
Methylene Chloride	None	104	None
Methyl Ethyl Keytone	16	176	IB
Pentane	<-40	97	IA
Petroleum Ether	<0	95-140	IA-IB
Propyl Alcohol	74	207	IC
n-Propyl Ether	70	194	IB
Pyridine	68	239	IB
Tetrahydrofuran	6	151	IB
Toluene	40	230	IB
Triethylamine	16	193	IB
m-Xylene	77	282	IC

Engineered Nanomaterials: Safe Research Practices

Nanoparticles are particles that have at least one dimension between 1-100 nanometers. These very small particles often possess radically different properties than larger particles of the same composition, making them of interest to researchers and of potential benefit to society. This fact sheet focuses on lab practices researchers should follow to protect themselves from the hazards of engineered nanoparticles.

Only limited information is currently available on the toxicity of nanoparticles. It is believed that some engineered nanoparticles may present health effects following exposure, based in part on air pollution studies that show smaller particles get deep into the lungs and can cause human illness. However, laboratory research most commonly involves handling nanoparticles in liquid solutions or other forms that do not become easily airborne, and even free-formed nanoparticles tend to agglomerate to a larger size.

When research involves work with engineered nanoparticles for which no toxicity data is yet available, it is prudent to assume the nanoparticles may be toxic, and to handle the nanoparticles using the laboratory safety techniques outlined below.

Potential Routes of Occupational Exposure to Researchers

There are four possible routes of workplace exposure to nanoparticles: inhalation, ingestion, skin absorption, and injection.

Inhalation. Respiratory absorption of airborne nanoparticles may occur through the mucosal lining of the trachea or bronchioles, or the alveolus of the lungs. Because of their tiny size, certain nanoparticles appear to penetrate deep into the lungs and may translocate to other organs following pathways not demonstrated in studies with larger particles. Thus, whenever possible, nanoparticles are to be handled in a form that is not easily made airborne, such as in solution or on a substrate.

Skin absorption. In some cases nanoparticles have been shown to migrate through skin and be circulated in the body. If the particle is carcinogenic or allergenic, even tiny quantities may be biologically significant. Skin contact can occur during the handling of liquid suspensions of nanoparticles or dry powders. Skin absorption is much less likely for solid bound or matrixed nanomaterials.

Ingestion. As with any material, ingestion can occur if good hygiene practices are not followed. Once ingested, some types of nanoparticles might be absorbed and transported within the body by the circulatory system.

Injection. Exposure by accidental injection (skin puncture) is also a potential route of exposure, especially when working with animals or needles.

Laboratory Safety Guidelines for Handling Engineered Nanoparticles

The current practices for working with engineered nanoparticles safely are essentially the same as one would use when working with any research chemical of unknown toxicity.

1. All personnel participating in research involving nanoscale materials need to be briefed on the potential hazards of the research activity, as well as on proper techniques for handling nanoparticles.
2. Wear gloves, safety glasses or goggles, and appropriate protective clothing.
3. Eating, drinking and chewing gum are not allowed in laboratories.
4. When purchasing commercially available nanoscale materials, be sure to obtain the Safety Data Sheet (SDS) and to review the information in the SDS with all persons who will be working with the material. Note, however, that given the lack of extensive data on nanoparticles, the information on an SDS may be more descriptive of the properties of the bulk material.
5. To minimize airborne release of engineered nanoparticles to the environment, nanoparticles should be handled in solutions, or attached to substrates so that dry material

is not released. Where this is not possible, nanoscale materials should be handled with engineering controls such as a HEPA-filtered local capture hood or glove box. If neither is available, work should be performed inside a fume hood.

6. Lab equipment and exhaust systems used with nanoscale materials should be wet wiped and HEPA vacuumed prior to repair, disposal, or reuse. Construction/maintenance crews should contact EH&S for assistance.
7. Spills of engineered nanoparticles are to be cleaned up right away.
8. Work surfaces should be wet-wiped regularly – daily is recommended. Because many engineered nanoparticles are not visible to the naked eye, surface contamination may not be obvious. Alternatively, disposable bench paper can be used.
9. All waste nanoparticles should be treated as unwanted hazardous "toxic" materials unless they are known to be non-hazardous. Dispose of and transport waste nanoparticles in solution according to hazardous waste procedures for the solvent. If you have questions on how to dispose a specific nanoparticle waste, call EH&S for more information.

PEROXIDE-FORMING COMPOUNDS

Peroxide Formation

Peroxide formation in common laboratory chemicals is caused by an autoxidation reaction. The reaction can be initiated by light, heat, introduction of a contaminant, or the loss of an inhibitor. Some chemicals have inhibitors such as BHT (2,6-di-tert-butyl-4-methyl phenol) hydroquinone and diphenylamine to slow peroxide formation. Most organic peroxide crystals are sensitive to heat, shock, or friction, and their accumulation in laboratory reagents has resulted in numerous explosions. For this reason, it is important to identify and control chemicals that form potentially explosive peroxides.

Peroxide-Forming Compounds

In general, the more volatile the compound, the greater its hazard, since the evaporation of the compound allows the peroxide to concentrate. Peroxide accumulation is a balance between peroxide formation and degradation. Some common compounds that are known to form peroxides are listed in the following table. NOTE: This is not an exhaustive list. Researchers must consult the SDSs and other sources of information for the chemicals used in their work areas to determine their peroxide-forming potential. Group A are chemicals that spontaneously form peroxides on exposure to air without further concentration or evaporation. These materials should be tested or disposed of within three months of opening (testing is discussed later in this section). Group B lists chemicals that form peroxides only upon concentration by evaporation or distillation. The materials in this list should be tested or disposed of within one year of opening their containers. Group C is a representative list of monomers that form peroxides that may act as a catalyst, resulting in explosive polymerization.

Group A: Chemicals That Form Explosive Levels of Peroxides Without Concentration

(Safe Storage Time After Opening: 3 Months)

Chemical	CAS	Synonyms	State
Butadiene(1,3)	106-99-0	1,3-Butadiene	G
Chloroprene (1,3)	126-99-8	2-Chloro-1,3- butadiene	L
Divinyl acetylene	821-08-9	1,5-Hexadien- 3-yne	L
Isopropyl ether	108-20-3		L
Tetrafluoroethylene	116-14-3		G
Vinyl ether	109-93-3	Divinyl ether	L
Vinylidene chloride	75-35-4	1,1- Dichloroethylene	L

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Group B: Chemicals That Form Explosive Levels of Peroxides on Concentration <u>(Safe Storage Time After Opening: 12 Months)</u>

Chemical	CAS	Synonyms	State
Acetal	105-57-7		L
Acetaldehyde	75-07-0		L
Benzyl alcohol	100-51-6		L
2-Butanol	78-92-2		l
Cyclohexanol	108-93-0		l
Cyclohexene	110-83-8		l
2-Cyclohexen-1-ol	822-67-3		l
Cyclopentene	142-29-0		l
Decahydronaphthalene	91-17-8		l
Diacetylene	460-12-8		g
Dicyclopentadiene	77-73-6		l
Diethylene glycol dimethyl ether	111-96-6	Diglyme	l
Dioxane	123-91-1	1,4-Dioxane	l
Ethylene glycol dimethyl ether	110-71-4	Glyme	l
Ethyl ether	60-29-7	Diethyl ether	l
Furan	128-37-0		l
4-Heptanol	589-55-9		l
2-Hexanol	626-93-7		l
Isopropyl benzene	98-82-8	Cumene	l
Methyl acetylene	74-99-7	Propyne	g
3-Methyl-1-butanol	123-51-3	Isoamyl alcohol	l
Methyl cyclopentane	96-37-7		l
Methyl isobutyl ketone	108-10-1	Methyl-i-butyl ketone	l
4-Methyl-2-pentanol	108-11-2		l
2-Pentanol	6032-29-7		l
4-Penten-1-ol	821-09-0		l
1-Phenylethanol	98-85-1	alpha-Methyl-benzyl alcohol	l
2-Phenylethanol	60-12-8	Phenethyl alcohol	l
2-Propanol	67-63-0	Isopropanol	l
Tetrahydrofuran	109-99-9		l
Tetrahydronaphthalene	119-64-2		L

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Group C: Chemicals That May Autopolymerize as a Result of Peroxide Accumulation

(Safe Storage Time After Opening: Inhibited Chemicals, 12 Months; Uninhibited Chemicals, 24 Hours)

Chemical	CAS	Synonyms	State
Acrylic acid(2)	79-10-7		l
Acrylonitrile(2)	107-13-1		l
Butadiene(1,3)	106-99-0		g
Buten-3-yne	689-97-4	Vinyl acetylene & Butenyne	g
Chloroprene(1,3)	126-99-8	2-Chloro-1,3-butadiene	l
Chlorotrifluoroethylene	79-38-9		g
Methyl methracrylate(2)	80-62-6		l
Styrene	100-42-5		l
Tetrafluoroethylene	116-14-3		g
Vinyl acetate	108-05-4		l
Vinyl chloride	75-01-4	Mono-chloroethylene	g
Vinylidene chloride	75-35-4	1,1-Dichloroethylene	l
2-Vinyl pyridine	100-69-6		l
4-Vinyl pyridine	100-43-6		l

Control Measures

- *Work Leads are responsible for identifying peroxide forming compounds used in the work area.*

Substitution and Chemical Inventory Management

- Identify and use safer chemical alternatives (e.g., chemicals that don't form peroxide crystals).
- Otherwise, procure chemicals that have a peroxide inhibitor added (e.g., BHT).
- If a safer chemical can't be used, limit what you buy.
- Conduct periodic cleanouts to prevent accumulating unneeded chemicals.
- Procure and use the minimum amount of material required for the operation.

Keep working quantities of chemicals to a minimum. Don't stockpile chemicals.

Engineering Controls

- A fume hood or other appropriate exhaust ventilation must be used when handling peroxide-forming chemicals in a manner that may produce an airborne hazard (such as fumes, gases, vapors, and mists). This includes procedures such as transfer operations, preparation of mixtures, blending, sonification, spraying, heating, evaporation and distilling.
- Place safety shields in front of reaction vessels, distillation columns and other apparatuses when fire, explosion or detonation may occur.
- Leave at least 10% bottoms when distilling peroxide-forming chemicals.

Personal Protective Equipment (PPE)

Skin and eye contact shall be prevented. The following PPE should be worn when handling these materials.

- At a minimum, safety glasses with side shields, laboratory coats and closed-toe shoes will be worn when handling these materials. This is to be considered as minimum protection.
- Additional PPE such as chemical goggles, face shields, chemical aprons, disposable coveralls, chemically resistant gloves and respiratory protection must be worn if there is a greater chance of chemical exposure.
- Gloves must be selected on the basis of their chemical resistance to the material(s) being handled, their suitability for the procedures being conducted, and their resistance to wear as well as temperature extremes. Improper selection may result in glove degradation, permeation of the chemical through the glove and ultimately personal exposure to the chemical. This is a potentially serious situation.

Storage

Consult the SDS section entitled Storage Guidelines for hazardous materials storage requirements, recommendations and information on chemical incompatibility. Additional requirements are provided below.

- Follow the storage guidelines for Flammable Liquids if the material is flammable.
- Store peroxide-forming chemicals in sealed, air-impermeable containers. Dark amber glass containers with tight-fitting caps are required. Do not use containers with loose-fitting lids or glass stoppers. These may allow the introduction of air and result in peroxide formation.

Safe Storage Times

- Table I provides safe storage times and peroxide- testing frequencies (see above).
- Storage for longer periods of time is allowable provided that testing is conducted at the indicated frequencies and that the results are within acceptable limits.

- Containers of unknown age or history, as well as those that have exceeded their shelf lives and that have no evidence of testing should not be opened or disturbed.

Disposal

If a peroxide-forming compound has been stored either beyond its useful shelf life, or if its age or history cannot be determined, it must be considered unsafe and should be disposed of as hazardous waste. Contact EHS for waste pickup. Write "Peroxide-forming Compound" on the form to alert EHS to the potential hazard. Contact EHS if you have questions regarding safety.

Labeling

- All materials should be dated when the container is received and when the container is first opened.
- The chemicals will be tested or disposed of according to the frequencies listed in Table 1.

Emergency Procedures

The following applies to spills of peroxide-forming compounds:

- Do not attempt to clean up peroxide former spills if there is any indication that these actions could initiate a detonation.
- Never use combustible or reactive materials (such as paper towels) to clean up or absorb spills of peroxide formers. Keep an adequate number of appropriate spill kits to meet anticipated needs. Typically, products containing diatomaceous earth are used for absorbing organic solvents.
- An emergency eyewash and safety shower should be located in all areas where chemicals are used. In the event of skin or eye contact, flush the affected area for at least 15 minutes. Seek medical attention if you deem it necessary.

Pyrophoric Materials

Pyrophoric and water reactive materials can ignite spontaneously or react violently on contact with air, moisture in the air, oxygen, or water. Failure to follow proper handling procedures can result in fire or explosion, leading to serious injuries, death, and/or significant damage to facilities. This document describes the hazards, proper handling, disposal and emergency procedures for working with pyrophoric and water reactive materials.

Any handling of a pyrophor/water reactive material is high risk and must be controlled with adequate system design, direct supervision, and training.

Examples of Pyrophoric/Water Reactive 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, lithium aluminum hydride
- Nonmetal hydrides: Diethylarsine, diethylphosphine
- Non-metal alkyls: R3B, R3P, R3As; tetramethyl silane, tributyl phosphine
- White and red phosphorus
- Group I (Alkali) metals: Lithium, potassium, sodium, sodium-potassium alloy (NaK), rubidium, cesium
- Gases: Silane, dichlorosilane, diborane, phosphine, arsine

Hazards

Because these reagents ignite/react violently on contact with air and/or water, they must be handled under an inert atmosphere and in such a way that rigorously excludes air/moisture. Some are toxic and many come dissolved or immersed in a flammable solvent. Other common hazards include corrosivity, teratogenicity, water reactivity, or peroxide formation, and may cause damage to the liver, kidneys, and central nervous system.

Controlling the Hazards

BEFORE working with pyrophoric or water reactive reagents, read the relevant Safety Data Sheets (SDS), technical bulletins, and guidance documents to understand how to mitigate the risks. The SDS must be reviewed before using an unfamiliar chemical and periodically as a reminder. Users of reactive materials must be trained in the laboratory-specific standard operating procedure and be able to demonstrate proficiency. Do not work alone or during off hours, when there are few people around to help. ALWAYS wear the appropriate personal protective equipment. Remove all excess and nonessential chemicals and equipment from the fume hood or glove box where pyrophoric or water reactive chemicals will be used. This will minimize the risk if a fire should occur. Keep combustible materials, including paper towels and Kimwipes, away from reactive reagents.

Keep the amount of pyrophoric or water reactive material present in your laboratory to the smallest amount practical. Use and handle the smallest quantity practical. It is better to do multiple transfers of small volumes than attempt to handle larger quantities (greater than 15 mL). Alternatively, an appropriately engineered system, capable of safely handling the larger quantity must be designed, tested, and properly used.

Personal Protective Equipment (PPE)

Eye Protection

- Indirectly vented chemical splash goggles are required when working with air/water reactive liquids.
- Prescription eye glasses and safety glasses will NOT provide adequate protection. A face shield that meets ANSI Z.87.1 1989, worn over splash goggles, is required any time there is a risk of explosion, splash hazard, or a highly exothermic reaction.
- All manipulations of pyrophoric chemicals which pose these risks must be carried out in a fume hood with the sash in the lowest feasible position or in a glove box.

Skin Protection

- Gloves must be worn when handling pyrophoric chemicals. Nitrile gloves should be adequate for handling most of these reagents in general laboratory settings but they are combustible. Use adequate protection to prevent skin exposures. Heavy gloves are required for work with larger quantities. A Nomex flight glove (used by pilots to protect from heat and flash), worn over disposable nitrile gloves, may be an option for work with larger quantities.
- **A fire retardant laboratory coat must be worn**. Special fire-resistant laboratory coats made from Nomex or other fire resistant materials are required. Laboratory coats must be buttoned and fit properly to cover as much skin as possible. Clothing, shirt and long pants, should be cotton or wool. Synthetic clothing is strongly discouraged.
- Appropriate shoes that cover the entire foot (closed toe, closed heel, no holes on the top) must be worn.

Safety Equipment

Researchers working with reactive materials must have the proper safety equipment and the emergency phone number (9-1-1) readily available for any emergencies, prior to starting research activities. Acceptable extinguishing media include soda ash, lime, Met-L-X, or dry sand to respond to fires. **DO NOT** use water to attempt to extinguish a pyrophoric/reactive material fire as it can actually enhance the combustion of some of these materials, e.g. metal compounds. A small beaker of Met-L-X, dry sand, lime, or soda ash 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. Review the SDS for the proper fire extinguisher to use with the given material.

Eyewash/ Safety Shower

- A combination eyewash/safety shower should be within 10 seconds travel time where reactive chemicals are used. Inside the laboratory is optimum.
- If a combination eyewash/safety shower is not available within the laboratory, an eyewash must be available (within 10 seconds travel distance) for immediate emergency use within the laboratory. Bottle type eyewash stations are not acceptable. A combination eyewash/shower must be available in the hallway or similar, within 10 seconds travel distance and accessible through only one door.
- Ensure that laboratory personnel know the locations of eyewashes and safety showers and the most direct route to access them.

Fume Hood

Many reactive chemicals release noxious or flammable gases upon decomposition and should be handled in a laboratory hood. In addition, some pyrophoric materials are stored under kerosene (or other flammable solvent); therefore the use of a fume hood (or glove box) is required to prevent the release of flammable vapors into the laboratory.

Glove (dry) box

Inert atmosphere glove boxes are an excellent device for the safe handling of reactive materials. Glove boxes used for this purpose should be in good working order and the moisture and oxygen levels of the atmosphere should be confirmed prior to introduction of reactive compounds into the box. Continuous monitoring of oxygen and moisture is highly recommended. Also, take into account interactions between items in the glove box (e.g., nitrogen is not an inert gas for lithium metal as the lithium is reduced violently to lithium nitride).

Gas Cabinets

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

Important Steps to Follow

Reactive reagents can be handled and stored safely as long as all exposure to atmospheric oxygen and moisture or other incompatible chemicals 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 and described below. Another good reference is "Manipulation of Air-sensitive Compounds" by Shriver and Drezdzon.

Handling Pyrophoric Liquids

Users must read, understand and follow manufacturer's recommendations The PI must also have in place laboratory-specific standard operating procedures for handling, storage, and disposal. Many of these reagents are stored at reduced temperature. Before accomplishing any transfer, let the reagent bottle warm to room temperature in the fume hood or glove box. Water vapor could condense on the needle surface which can initiate ignition. Be sure to wipe any moisture off the bottle and septum.

Syringe Transfer

Luer-lock disposable Teflon syringes are recommended, rather than glass syringes, as they have a better seal. Non-disposable syringes and needles should be cleaned, dried in an oven and left to cool in a desiccator to avoid absorption of water upon cooling. Be sure to cool all equipment to room temperature before attempting transfer. Clamp reagent bottle firmly before beginning transfer. Attach a balloon of inert gas or an inert gas line through the septum to keep positive pressure in the reagent bottle during the transfer, keeping the needle tip out of the liquid. Flush the syringe and needle three times with inert gas. In the last flush, fill the headspace of the reagent bottle with some inert gas, then quickly insert the needle into the reagent bottle. Firmly hold the syringe plunger and very slowly fill the syringe by gently pulling the plunger up. NEVER fill a syringe to more than ¾ capacity. By bending the long needle and holding the needle in the septum, tip the syringe upside down and slowly force any excess reagent and bubbles back into the reagent bottle. Pull the needle tip up out of the liquid and draw a plug of inert gas from the reagent bottle headspace into the needle. Holding the syringe barrel in place, slowly pull the needle out of the septum. Quickly insert the needle into a septum-sealed receiver flask. Slowly deliver the measured volume into the receiver flask –drop wise, if there's evolution of gas or increase in reaction behavior. Be sure the pressure inside the receiver flask is equalized. Double-
For extended storage of unused reagents, use the solid plastic cap, equip the bottle with an Oxford Sure/Seal valve cap, or transfer the reagent to a suitable storage vessel, as described below.

Storage and Disposal

Storage

- Use and store minimal amounts of reactive chemicals. Do not store reactive chemicals with flammable materials or in a flammable liquids storage cabinet. Secondary containers carrying reactive materials must be clearly labeled with the correct chemical name, in English, and hazard warning.
- Store reactive materials as recommended in the SDS. An inert gas-filled desiccator or glove box is suitable storage locations for most materials.
- 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 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 any new empty containers thoroughly
- Insert the septum into the 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. To introduce the excess chemical, use the procedure described in the handling section, below.
- For long-term storage, the septum should be secured with a copper wire.

Disposal of Pyrophoric Reagents

- Any container with a residue of reactive materials must never be left open to the atmosphere.
- Any unused or unwanted reactive materials must be destroyed by transferring the materials to an appropriate reaction flask for hydrolysis and/or neutralization with adequate cooling.
- The empty container should be rinsed three times with an inert dry COMPATIBLE 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.
- The empty container, solvent rinses and water rinse must be disposed as hazardous waste and must not be mixed with incompatible waste streams.

Disposal of Pyrophoric or Water Reactive Contaminated Materials

- All materials – disposable gloves, wipers, bench paper, etc. - that are contaminated with pyrophoric chemicals must be disposed as hazardous waste. Proper and complete hazardous waste labeling of containers is vital.
- The contaminated waste must not be left overnight in the open laboratory but must be properly contained to prevent fires.

Emergency Procedures

Spill

- **DO NOT** use water to attempt to extinguish a reactive material fire as it can actually enhance the combustion of some reactive 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 reactive compound. Met-L-X, soda ash, lime, or dry sand should be used to completely smother and cover any small spill that occurs.
- A container of Met-L-X, soda ash, powdered lime, or dry sand should be kept within arm's reach when working with a reactive material.
- If anyone is exposed, or on fire, wash with copious amounts of water, preferably under a safety shower.
- If metal compounds are involved, smothering the fire is a better course of action.
- The recommended fire extinguisher is a standard dry powder (ABC) type. Class D extinguishers are recommended for combustible solid metal fires (e.g, sodium, potassium), but not for organolithium reagents. Contact Fire Prevention and review the SDS for the appropriate fire extinguisher.
- Call 9-1-1 for emergency assistance and for assistance with all fires, even if extinguished.
- Pyrophoric gas releases and associated fires, should be extinguished by remotely stopping the gas flow. NEVER ATTEMPT TO PUT OUT A GAS FIRE IF THE GAS IS FLOWING.

Fume Hoods

One of the most important safety devices in a laboratory is a properly functioning fume hood. The fume hood protects users by containing and exhausting airborne hazards; it does this by constantly pulling room air into the hood and exhausting it from the roof. Fume hood sashes also provide shielding in the event of an explosion or fire inside the hood.

A fume hood should be used in the following situations:

- When working with chemicals with significant inhalation hazards, such as hazardous chemical vapors, volatile radioactive materials, toxic gases or reparable toxic powders
- When carrying out procedures that could explode or generate high pressure
- When chemical vapors generated could cause a fire hazard
- When working with compounds that have an offensive odor

Keep all work at least 6 inches inside of the hood. The capture ability of a fume hood may not be 100% at the front edge of the hood because of air turbulence. Working with hazardous materials further toward the back of the hood is safest.

Minimize storage. Do not take up hood space and block ventilation by storing unused equipment or chemicals in hoods. If large items must be kept in the hood, contact EHS.

Never lean your head inside the fume hood when hazardous chemicals are present.

Close the sash when the hood is not being used.

Prevent air pollution. The chemical vapors generated in most hoods are exhausted untreated into the atmosphere. To minimize pollution, seal all chemical containers not in use. Never use the hood to evaporate excess chemical waste. By law, all chemical containers must be capped when the hood is not operating.

Keep the hood clean. Remove unneeded experimental glassware and clutter. Wipe-up spilled chemicals or residues. Make sure you can see through the glass sash, and that the light in the hood works.

Do not heat perchloric acid ($HClO_4$) in standard fume hoods. Perchloric acid vapors may create explosive perchlorates in the duct work. Contact EHS if you are performing perchloric acid digestions. There are a few special hoods on campus that are specifically engineered for the use of perchloric acid. These hoods have a special water wash-down feature that needs to be used if perchloric acid vapors are generated.

CHEMICAL SPILL RESPONSE

Despite the best efforts of the USD community to practice safe science in the laboratory, accidents resulting in the release of chemicals will occur.

SPILL RESPONSE PROCEDURES--Major Spill

In the event of a spill which: 1) involves the release of a type or quantity of a chemical that poses an immediate risk to health; or 2) involves an uncontrolled fire or explosion:

- Evacuate the building by activating the nearest fire alarm.
- Call 911 and give details of the accident including location, types of hazardous materials involved, and whether there is personal injury.

If the accident involves personal injury or chemical contamination, follow the above steps as appropriate and at the same time:

- Move the victim from the immediate area of fire, explosion, or spill (if this can be done without further injury to the victim or you).
- Locate nearest emergency eyewash or safety shower. Remove any contaminated clothing from the victim and flush all areas of the body contacted by chemicals with copious amounts of water for 15 minutes.
- If you are First Aid/CPR Certified, administer first aid as appropriate and seek medical attention.

SPILL RESPONSE PROCEDURE--Minor Spill

In the event of a spill involving the release of a type or quantity of a chemical which does not pose an immediate risk to health and does not involve chemical contamination to the body:

1. Notify lab personnel and adjoining personnel of the accident.
2. Isolate the area. Close lab doors and evacuate the immediate area if necessary.
3. Remove ignition sources and unplug nearby electrical equipment.
4. Establish exhaust ventilation. Vent vapors to outside of building only (open windows and turn on fume hoods).
5. Locate spill kit.
6. Choose appropriate personal protective equipment (goggles, face shield, gloves, lab coat, etc.)
7. Confine and contain spill. Cover with appropriate absorbent material. Acid and base spills should be neutralized prior to cleanup. Sweep solid material into a plastic dust pan and place in a sealable 5 gallon container.
8. Wet mop spill area. Be sure to decontaminate broom, dustpan, etc. Put all contaminated items (gloves, clothing, etc.) into a sealable 5 gallon container or plastic bag. Call EH&S if a special pickup is necessary.

Particularly Hazardous Substances

Use, handling and storage of most chemicals will follow standard methods outlined in this manual. Some chemicals, however, require special methods to ensure safety. A Particularly Hazardous Substance (PHS) is a chemical with a greater degree of toxicity or reactivity. USD requires an SOP (Standard Operating Procedure) for use of chemicals that are identified as PHS's.

The EHS Department has reviewed chemical inventory lists at USD and has made initial determinations about what chemicals are PHS's. We have compiled this information in a spreadsheet that lists chemical name, Chemical Abstract Service (CAS) Number, as well as criteria on which the status is based (carcinogen, reproductive toxin, and acute toxicity, reactivity). This list is not all inclusive. If your laboratory contains a chemical that you believe should be identified as a PHS, please forward this information to EHS for inclusion on the list. If you are unsure, call the EHS Office for assistance.

Glassware Use

Broken glass is one of the most common causes of laboratory injuries. To reduce the chance of cuts or punctures, be careful when working with glassware. Inspect glassware for chips and cracks before use.

- Discard or repair any chipped or cracked items
- Never use laboratory glassware to serve food or drinks
- Use care in handling and storing glassware to avoid damaging it
- Leave an air space of at least 10% in containers with positive closures
- Thoroughly clean and decontaminate glassware after each use
- When inserting glass tubing into rubber stoppers, corks, or tubing, use adequate hand protection (e.g., gloves or a towel), lubricate the tubing and hold hands close together to minimize movement if the glass breaks
- Use thick-walled, round-bottomed glassware for vacuum operations. Flat-bottomed glassware is not as strong as round-bottomed glassware. Carefully handle vacuum-jacketed glassware to prevent implosions. Dewar flasks, vacuum desiccators, and other evacuated equipment should be taped or shielded and for vacuum work; use only glassware designed for that purpose.
- Large glass containers are highly susceptible to thermal shock. Heat/cool large glass containers slowly. Use Pyrex or heat-treated glass for heating operations

With proper precautions, work with glassware can be conducted safely. These additional handling precautions will help reduce the risk of injury.

- When handling cool flasks, grasp the neck with one hand and support the bottom with the other hand
- Lift cool beakers by grasping the sides just below the rim. For large beakers, use two hands, one on the side and one supporting the bottom
- Never carry bottles by their necks or by the caps.
- Use a cart to transport large bottles of dense liquid

Regardless of the precautions you take, glass may still break. Broken glass poses a hazard for puncture wounds and injection of hazardous chemicals.

- Do not pick up broken glass with bare or unprotected hands. Use a brush and dustpan to clean up broken glass. Remove broken glass in sinks by using tongs for large pieces and cotton held by tongs for small pieces and slivers
- Dispose of broken glass and other sharps according to University policy

Frozen Glass Stoppers. Ground glass stoppers frozen by contact with base solutions may be welded shut. Be careful when removing frozen glass stoppers. First, try soaking the stopper in hot water to expand the glass. If you need to remove a stopper by tapping, wrap the stopper in a cloth or paper towel and wear gloves to protect your hands and prevent injury in case of breakage.

Refrigerators and Freezers

Using a household refrigerator to store laboratory chemicals is hazardous for several reasons. Many flammable solvents are still volatile at refrigerator temperatures. Refrigerator temperatures may be higher than the flash point of a flammable liquid. Additionally, the storage compartment of a household refrigerator contains numerous potential ignition sources including thermostats, light switches, etc. Furthermore, the compressor and electrical circuits are located at the bottom of the unit, where chemical vapors are likely to accumulate, and are not sealed. Laboratory-safe and explosion-proof refrigerators typically provide adequate protection for chemical storage in the laboratory. For example, laboratory-safe refrigerators are specifically designed for use with flammables, with the sparking components located on the exterior of the refrigerator. Explosion-proof refrigerators are required in areas that may contain high levels of flammable vapors. These guidelines will help insure safety:

- Never store flammable chemicals in a household refrigerator
- Do not store food or drink in a laboratory refrigerator/freezer
- Ensure that all refrigerators are clearly labeled to indicate suitable usage
- Laboratory-safe and explosion-proof refrigerators are identified by a manufacturer label
- Refrigerators used to hold food should be labeled, “For Food Only”

Heating Systems

Next to glass failure, the most common source of laboratory injury is the improper manipulation of heating apparatus. The following systems are sources of heat used in laboratory procedures:

- Open flame burners
- Hot plates
- Heating mantles
- Oil baths
- Hot air guns
- Ovens and Furnaces
- Microwave ovens

Some laboratory heating procedures involve an open flame. Common hazards associated with laboratory heating devices include electrical hazards, fire hazards, and hot surfaces. When temperature of 100 C (212 F) or less are required, it is safer to use a steam-heated device than an electrically heated device as electrically heated devices can present a shock or spark hazard. Steam-heated devices can also be left unattended with the assurance that their temperature will never exceed 100 C (212 F). Follow these guidelines when using heating devices:

Before using any electrical heating device, ensure that the heating unit is in good working condition and has an automatic shutoff to protect against overheating

Heated chemicals can cause more physical damage faster than the same chemical would cause at a lower temperature. Exercise an enhanced degree of caution when working with heated chemicals.

Heating baths should be equipped with timers to insure that they turn on and off at appropriate times

Use a chemical fume hood when heating flammable or combustible solvents. Arrange the equipment so that escaping vapors do not contact heated or sparking surfaces

Use non-asbestos thermal-heat resistant gloves to handle heated materials and equipment

Do not leave oil baths unattended. Place your oil bath within a plastic or metal tray to contain any spills

Minimize the use of open flames. It is a good idea to connect all exit ports from gas chromatographs (GC), atomic absorption (AA) spectrometers, and other analytical instruments to an exhaust ventilation system to exhaust toxic contaminants from the laboratory.

Vacuum Systems

Vacuum systems may be as hazardous as pressurized systems. Vacuum lines and other glassware at sub-ambient pressure may implode, causing a flying glass hazard. Dangers are also associated with possible toxic chemicals contained in the system. Use these precautions:

- Ensure that pumps have belt guards in place during operation
- Ensure the service cords and switches are free from defect
- Always use a trap on vacuum lines to prevent liquids from being drawn into the pump, house vacuum line, or water drain
- Replace and properly dispose of vacuum pump oil that is contaminated with condensate
- Place a pan under pumps to catch oil drops
- Do not operate pumps near container of flammable chemicals
- Do not place pumps in an enclosed, unventilated cabinet

Glassware used in vacuum operations may pose a hazard if it breaks. To reduce the injury from glass debris:

- Only heavy-walled round bottomed glassware should be used for vacuum operations. The only exception is glassware specifically designed for vacuum operations (e.g., Erlenmeyer filtration flask)
- Wrap exposed glass with tape to prevent flying glass if an implosion occurs
- Carefully inspect vacuum glassware before and after each use. Discard any glass that is chipped, scratched, broken, or otherwise stressed

Glass desiccators may develop a slight vacuum due to contents cooling. When possible, use molded plastic desiccators with high tensile strength. For glass desiccators, use a perforated metal desiccator guard.

Vacuum pumps may have a cold trap in place to prevent volatile compounds from getting into hot pump oil and vaporizing into the atmosphere and to prevent moisture contamination in a vacuum line. Guidelines for using a cold trap include:

- Locate the cold trap between the system and vacuum pump
- Ensure the cold trap is big enough and cold enough to condense vapors present in the system
- Check frequently for blockages in the cold trap
- Use isopropanol/dry ice or ethanol/dry ice instead of acetone/dry ice to create a cold trap. Isopropanol and ethanol are cheaper, less toxic, and less prone to foam
- Do not use dry ice or liquefied gas refrigerant bath as a closed system; these can create uncontrolled and dangerously high pressures

Compressed Gas Cylinders

Compressed gas cylinders are used in many research and support activities on campus. Cylinders present significant hazards due to high pressure gases contained within the cylinders. Persons using or handling cylinders should have basic training on-file with their department or supervisor. At a minimum, this training should include review of operating and safety protocols for tasks to be performed, review of appropriate Material Safety Data Sheets (MSDS), and hands-on training by an experienced gas cylinder user. This document presents general guidelines for use, transport and storage of gas cylinders.

Using and Transporting Gas Cylinders

- Read the label on the cylinder before connecting a new cylinder of compressed gas. If the label is illegible or missing, return the cylinder to the supplier. Don't rely on stenciling or color of the cylinder. Do not use a cylinder with unidentified contents.
- Keep cylinders upright. Never lay cylinders on their sides, particularly those containing flammable gases.
- If a gas cylinder valve is damaged, the contents can exit with great force. Cylinders propelled by their contents may penetrate cinder block walls. Cylinders should be affixed via two brackets to a permanent building fixture such as a bench or wall during use or storage. Brackets that can be screwed into the mounting surface are preferred over clamp-type brackets. If you need cylinder brackets permanently attached to the wall contact EHS. When the cylinder has no regulator attached and is not in service, replace the valve cover and screw it on hand tight.
- Transport cylinders larger than lecture bottle size with a hand truck or cylinder cart. Rolling or "walking" cylinders is extremely hazardous. Never transport a cylinder with a regulator attached! Always protect the valve during transport by replacing the valve cover. Select a regulator recommended for use with your cylinder. The pressure, purity, and corrosive properties of the gas will determine the correct regulator. Never attempt to use a cylinder without a regulator or some other pressure-reducing device in place.
- When preparing to withdraw gas from a high-pressure cylinder, close the regulator first. Open the main cylinder valve until it stops and adjust the gas flow rate using the regulator. For cylinders containing fuel gases, open the cylinder valve one-quarter turn, adjusting the regulator as above.
- When you are finished using a compressed gas system, turn off the main cylinder valve, bleed the regulator and lines, and close the regulator. Do not leave the regulator under pressure by closing down flow from the regulator without shutting off the main cylinder valve. Be sure to LOCKOUT upstream gas lines leading to equipment prepared for maintenance. Compressed gases are a hazardous energy source requiring lockout/tagout procedure. Adequately purge lines following lockout procedures and before beginning maintenance.

- Do not drain a cylinder completely. Air can be sucked back through the valve, contaminating the cylinder or creating an explosive mixture.

Precautions For Specific Gases

- Consult the Safety Data Sheet for all gases used. Some gases are corrosive (hydrogen chloride), toxic (ethylene oxide), anesthetic (nitrous oxide), or highly reactive (anhydrous ammonia).
- Flammable gases such as propane, hydrogen, and acetylene always have a red label. However, the color of the cylinder itself is not a good indicator of flammability as different distributors may use different colored cylinders for the same gas. Check the label for flammability.
- Hazardous/toxic gas (arsine, carbon monoxide, hydrogen, phosgene, phosphine, etc.) cylinders should be stored in a suitable exhausted location or gas cabinet.
- Inert gases, such as nitrogen and carbon dioxide must be treated with caution. If left to leak into a closed space, these gases may displace oxygen and create a risk of asphyxiation.
- Compressed oxygen, while not combustible itself, will cause many materials to burn violently. Never use grease, solvents, or other flammable material on an oxygen valve, regulator, or piping. Oxygen cylinder regulators are purpose-designed and won't fit on cylinders of other gases.
- Toxic, corrosive, and pyrophoric gases have special handling and storage requirements. Contact EH&S if you plan to use these gasses.

Gas Cylinder Storage

Store cylinders in a well-ventilated area away from ignition sources. Fuel gases must never be stored in an enclosed area, such as a closet. Never store cylinders under stairways or in hallways designated for emergency exit. Store oxygen cylinders at least twenty feet from flammable gas cylinders. If this cannot be done, consult EHS for guidance. Mark empty cylinders, close their valves, and segregate them from full cylinders. Protect the valves by installing the valve caps. For outdoor storage, provide drainage, overhead cover, and security.

UNIVERSITY OF SOUTH DAKOTA

USD Laboratory Safety Inspection Form

Building & Room #: ________________ Department: __________________ Date:_____
Supervisor: ________________________ Inspector:______________________________

Criteria	YES	NO	N/A
Emergency Equipment			
Means of egress / exits clear and unobstructed			
Fire extinguishers in designated locations, accessible and unobstructed			
Safety Showers / Eyewashes labeled, accessible, free from obstructions, tested			
First aid kit available, maintained (i.e., no oral drugs)			
Personal protective equipment (PPE) available, appropriate to hazard and used			
Shoes, long pants, lab coats, glasses (i.e., protective clothing) worn when working in labs			
Spill kit available			
Emergency procedures posted			
Signs / Labels			
Emergency Contact List posted			
Refrigerators / freezers labeled "No Food & Drink" "No Flammables" or "Food & Drink Only"			
Biohazard / Radioactive Materials signs posted			
Other signs required (e.g., laser, magnets, bright light, etc.)			
Electrical Equipment			
Electric cords in good condition, no exposed wiring			
Ground Fault Circuit Interrupters (GFCI) in wet or high humidity areas			
Equipment properly grounded (e.g., ground plugs), 2-prong appliances not near sinks			
Extension cords for temporary use and cords / power strips not daisy chained			
Electrical panels free of obstructions			
Fume Hoods / Biological Safety Cabinets (BSC) / Laminar Flow Hoods			
Fume hoods, BSC, laminar flow hoods certified (dates:			
Hood sashes open / close properly and glass is intact			
Sash kept at 18" height while working and closed when not in use			
Hood kept running at all times			
Equipment used inside hood properly positioned / free of excess equipment			
Hood not used to store equipment, chemicals, nor waste			
Special purpose hoods (e.g., perchloric)			
Hazardous Material			
Chemical inventory available and up-to-date / updated annually			
Chemicals dated & initialed on receipt			
Chemical containers labeled with name of contents, capped and in good condition			
Corrosive chemicals stored below eye level			
Chemicals segregated by hazard (e.g., organics away from oxidizers, flammables from acids)			
Highly reactive chemicals stored in chemical-safe refrigerator			
Flammable solvents stored in approved safety cans or solvent storage cabinets			
No combustibles stored within 3 feet of the ceiling			
Secondary containers used to transport chemicals outside the lab			
Hazardous materials near sinks / drains inside secondary containers			
Compressed Gas Storage			
Gas cylinders properly marked, stored / secured in upright position			
Stored cylinders tightly capped & kept to minimum			

Criteria	YES	NO	N/A
Regulators, connections and tubing in good condition, valves closed with not in use			
Complies with NFPA (i.e., max of 3 flammable, oxygen / health hazard cylinders per 500 sq ft)			
For toxic gases, leak sensors / alarms in place, regularly checked and calibrated			
Training / Documentation / Publications			
Laboratory workers trained / instructed in potential hazards and lab safety practices			
Lab specific training (SOPs, chemical segregation, equipment handling, etc.) documented			
Copy of all safety manuals (Radiation, Chemical, biological) available			
SDSs available, updated, accessible (CD or hard copy)			
Laboratory workers received chemical / waste training			
All personnel in lab completed annual refresher training			
Hazardous Waste Management			
Waste containers labeled and chemical compositions identified			
Broken glassware, sharps, pipette tips segregated and properly disposed			
Waste stored in secondary containment			
Chemical waste stored in a “designated” area			
Biohazard containers properly used where needed (e.g., autoclave bags, sharps containers)			
Biological Safety Issues			
Biological and/or infectious agents in use (RG)			
Biological use authorizations on file and current			
Laboratory furniture appropriate and easily decontaminated			
Biological waste bags with biohazard symbol in hard-sided, closed container			
Autoclave use log available / current and autoclaves tested after 40 hours of combined use			
Bloodborne pathogen program (workers trained & offered vaccinations - documented)			
Radiation Safety Issues			
NRC form 3 posted and Caution Radioactive Materials signs / labels used			
Absorbent paper used on work surfaces			
Radiation survey meter available and calibrated (date:)			
Radioisotope inventories available and current			
Radiation survey performed monthly and contamination cleaned			
Radiation dosimeters used, if appropriate			
Radioactive waste segregated by isotope, labeled, activity recorded			
Radiation survey of work area performed at conclusion of procedure			
Lasers, UV, RF sources (Laser Class)			
Vacuum Equipment			
Glass Dewars wrapped / shielded			
Vacuum pump belt guards in place			
Protective shatterproof shields used when vacuum equipment used.			

Comments:

Discussed results with lab PI / supervisor