

GENERAL LABORATORY SAFETY PROCEDURES

DO

- Know the potential hazards of the materials used in the laboratory. Review the Material Safety Data Sheet (MSDS) and container label prior to using a chemical.
- Know the location of safety equipment such as emergency showers, eyewashes, fire extinguishers, fire alarms, spill kits, first aid kits, and telephones.
- Review emergency procedures to ensure that necessary supplies and equipment for spill response and other accidents are available.
- Practice good housekeeping to minimize unsafe work conditions such as obstructed exits and safety equipment, cluttered benches and hoods, and accumulated chemical waste.
- Wear personal protective apparel when working with chemicals. This includes eye protection, lab coat, gloves, and appropriate foot protection (no sandals). Gloves should be made of a material known to be resistant to permeation by the chemical in use.
- Wash skin promptly if contacted by any chemical, regardless of corrosivity or toxicity.
- Label all new chemical containers with the “date received” and “date opened.”
- Label and store chemicals properly. All chemical containers should be labeled to identify the container contents (no abbreviations or formulas) and hazard information. Chemicals should be stored by hazard groups and chemical compatibilities.
- Use break-resistant bottle carriers when transporting chemicals in glass containers that are greater than 500 milliliters.
- Use fume hoods when processes or experiments may result in the release of toxic or flammable vapors, fumes, or dusts.

DON'T

- Eat, drink, chew gum, or apply cosmetics in areas where chemicals are used and stored.
- Store food in laboratory refrigerators, ice chests, cold rooms, or ovens.
- Drink water from laboratory water sources.
- Use laboratory glassware to prepare or consume food.
- Smell or taste chemicals.
- Pipet by mouth.
- Work alone in the laboratory without prior approval from the lab supervisor.
- Leave potentially hazardous experiments or operations unattended without prior approval from the lab supervisor. In such instances, the lights in the laboratory should be left on and emergency phone numbers posted at the laboratory entrance.

**FOR CHEMICAL SAFETY ASSISTANCE CALL
ENVIRONMENTAL HEALTH AND SAFETY:**

**(812) 855-6311
(8a.m.-5p.m., Mon.-Fri.)**

PROCEDURES FOR PROPER LABELING, STORAGE, AND MANAGEMENT OF CHEMICALS

Proper chemical labeling and storage is essential for a safe laboratory work environment. Inappropriate storage of incompatible or unknown chemicals can lead to spontaneous fire and explosions with the associated release of toxic gases. To minimize these hazards, chemicals in the laboratory must be segregated properly. The storage procedures listed below are not intended to be all-inclusive but should serve instead, to supplement more specific procedures and recommendations obtained from container labels, Material Safety Data Sheets (MSDSs), and other chemical reference material. For more information about chemical storage contact the University Office of Environmental Health and Safety (855-6311).

LABELING

- Manufacturer chemical labels should never be removed or defaced until the chemical is completely used.
- All chemical and waste containers should be clearly labeled with the full chemical name(s) (no abbreviations or formulas) and appropriate hazard warning information. Small containers that are difficult to label such as 1-10 ml vials and test tubes can be labeled as a group and stored together. Unattended beakers, flasks, and other laboratory equipment containing chemicals used during an experiment should be labeled with the full chemical name(s).
- All chemicals should be labeled with the “date received” and “date opened.”
- All hazardous waste containers must be labeled with the words “hazardous waste.”
- All hazardous waste containers must be marked with an accumulation date. The accumulation date represents the date that the container becomes full (waste containers should NOT be filled to more than 90% of their capacity). All full waste containers should be disposed of promptly.
- All chemical storage areas such as cabinets, shelves and refrigerators should be labeled to identify the hazardous nature of the chemicals stored within the area (e.g., flammables, corrosives, oxidizers, water reactives, toxics, carcinogens, and reproductive toxins). All signs should be legible and conspicuously placed.

STORAGE

HAZARD GROUPS

- | | |
|---|---|
| <ul style="list-style-type: none"> ◦ Flammable/Combustible Liquid ◦ Flammable Solids ◦ Inorganic Acids ◦ Oxidizing Acids (Nitric, etc.) ◦ Organic Acids ◦ Caustics (Bases) ◦ Oxidizers ◦ Water Reactives ◦ Air Reactives | <ul style="list-style-type: none"> ◦ Unstable (Shock-sensitive, Explosive) ◦ Carcinogens, Reproductive Toxins ◦ Toxic, Poisonous ◦ Non-Toxic ◦ Gases <ul style="list-style-type: none"> - Toxic - Flammable - Oxidizers and Inert - Corrosive |
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PROCEDURES FOR PROPER LABELING, STORAGE, AND MANAGEMENT OF CHEMICALS (continued)

- A definite storage place should be provided for each chemical and the chemical should be returned to that location after each use.
- Chemical containers should be in good condition before they are stored. Containers should be managed to prevent leaks.
- Maximum quantities of chemicals that can be in storage and use in laboratories are found in the *Uniform Building Code*¹, the *Uniform Fire Code*², the *International Building Code*³ and *International Fire Code*⁴. The tables maximum allowable quantities are found in Appendix C. Laboratories constructed prior to 2003 must comply with the requirements of the *Uniform Building and Fire Codes*. Laboratories constructed during or after 2003 must comply with the requirements of the *International Building and Fire Codes*. These codes place specific requirements on storage facilities for all hazard classes and some are very low such as highly toxic gasses and organic peroxides.
- Chemicals (including waste) should be separated and stored according to their hazard group and specific chemical incompatibilities. Chemicals within the same hazard group can be incompatible and therefore it is important to review the chemical label and MSDS to determine the specific storage requirements and possible incompatibilities. Appendix C contains a partial list of incompatible chemicals.
- Special attention should be given to the storage of chemicals that can be classified into two or more hazard groups. For example, acetic acid and acetic anhydride are both corrosive and flammable. In addition, perchloric acid is both corrosive and a strong oxidizer. Refer to the MSDS for proper storage procedures.
- Chemicals should be separated by distance. Physical barriers such as storage cabinets and secondary containers should be used to prohibit contact of incompatible chemicals in the event that they are accidentally released or spilled.
- Secondary containers are highly recommended for the storage of liquid chemicals. Secondary containers should be made of a material that is compatible with the chemical(s) it will hold and should be large enough to contain the contents of the largest container.
- Liquid chemicals should not be stored above dry chemicals unless they are stored in secondary containers.
- Storage of chemicals within hoods and on bench tops should be avoided.
- Stored chemicals should not be exposed to heat or direct sunlight.
- Storage shelves and cabinets should be secure to prevent tipping. Shelving should contain a front-edge lip or doors to prevent containers from falling.
- Flammable and corrosive storage cabinets should be used when possible.
- Flammable liquids in quantities exceeding a total of 10 gallons in each laboratory must be stored in an approved flammable storage cabinet.
- Only explosion-proof or laboratory-safe refrigerators may be used to store flammable liquids.
- Liquid chemicals should be stored below eye level to avoid accidental spills.
- Chemicals should not be stored in areas where they can be accidentally broken and spilled such as on the floor or on the edge of a bench top.
- Chemicals should not be stored in areas where they obstruct aisles, exits, and emergency equipment.

PROCEDURES FOR PROPER LABELING, STORAGE, AND MANAGEMENT OF CHEMICALS

(continued)

CHEMICAL INVENTORY MANAGEMENT

All chemicals should be inventoried especially high risk chemicals. Inventories provide a method of tracking chemicals for ordering and re-ordering, waste disposal, compliance with building and fire codes, hazard communication, community right-to-know requirements, and to track dangerous or time sensitive chemicals for safety and security reasons.

Inventories should contain all pertinent information including the following data:

- Chemical name (synonym or trade name found on the MSDS), if mixture list composition and percent of components.
- Chemical Abstract Service (CAS) number.
- Manufacturer.
- Product number.
- Physical state.
- Hazard class.
- Container size.
- Units of measure.
- Quantity or number of containers.
- Principal investigator, lab supervisor, or chemical hygiene officer.
- Owner or researcher.
- Location (i.e. building, room number, cabinet).
- Receiving date.
- Opened container date.
- Expiration date.

Other information can be recorded as necessary such as cost for accounting purposes. Expiration dates are of particular importance for time-sensitive chemicals that can become dangerous with age. Several noteworthy time sensitive laboratory chemicals include:

- Chemicals that form peroxides.
- Picric acid and other multi-nitro aromatics.
- Chloroform.
- Anhydrous hydrogen fluoride and hydrogen bromide.
- Liquid hydrogen cyanide.
- Formic acid.
- Alkali metals (K, Na, Li).

See section 3.17, Handling and Management of Peroxide Forming Chemicals and Other Time Sensitive Materials.

PROCEDURES FOR PROPER LABELING, STORAGE, AND MANAGEMENT OF CHEMICALS (continued)

The following guidelines can be used to manage all laboratory chemicals including time sensitive materials:

Acquisition control.

- Do not hoard chemicals.
- Do not over purchase quantities.
- Use just in time purchasing whenever possible.
- Dispose of unused portions.

Research the literature and MSDS information.

- Define storage conditions.
- Consider refrigeration requirements or other storage options.
- Consider chemical incompatibilities.

Define “unsafe” conditions such as:

- Temperature or humidity extremes.
- Peroxide concentrations greater than 100 ppm.
- Dry picric acid.
- Expiration dates.

Track Laboratory Chemicals.

- Maintain an accurate chemical inventory and check expiration dates regularly.
- Define inspection interval for each chemical.
- Log the date of inspection and re-inspect without fail.

Manage Expired or “Unsafe” Chemicals.

- Never place chemicals where they will become lost or forgotten.
- Do NOT touch lost time sensitive chemicals. Call EH&S immediately (855-6311).

References: 1. *Uniform Building Code*, 1997, Section 307, Requirements for Group H Occupancies.
2. *Uniform Fire Code*, 1997, Article 80, Hazardous Materials.
3. *International Building Code*, 2000, Section 307, High-Hazard Group H
4. *International Fire Code*, 2000, Chapter 27, Hazardous Materials-General Provisions
5. *Journal of Chemical Health and Safety*, Management of Time Sensitive Chemicals, p. 14-17, Vol. 11, No. 5, September/October 2004.

CHEMICAL FUME HOODS PROCEDURES FOR PROPER AND SAFE USE

Chemical fume hoods are one of the most important items of safety equipment present within the laboratory. Chemical fume hoods serve to control the accumulation of toxic, flammable, and offensive vapors by preventing their escape into the laboratory atmosphere. In addition, fume hoods provide physical isolation and containment of chemicals and their reactions and thus serve as a protective barrier (with the sash closed) between laboratory personnel and the chemical or chemical process within the hood.

- A chemical fume hood should be used for any chemical procedures that have the potential of creating:
 1. Airborne chemical concentrations that might approach Permissible Exposure Limits (PELs) for an Occupational Safety and Health Administration (OSHA) regulated substance. These substances include carcinogens, mutagens, teratogens, and other toxics (see Appendix A and C).
 2. Flammable/combustible vapors approaching one tenth the lower explosion limit (LEL). The LEL is the minimum concentration (percent by volume) of the fuel (vapor) in air at which a flame is propagated when an ignition source is present.
 3. Explosion or fire hazards.
 4. Odors that are annoying to personnel within the laboratory or adjacent laboratory/office units.
- The hood sash opening should be kept to a minimum while the hood is used. When working with hazardous chemicals, the hood sash should be positioned so that it acts as a protective barrier between laboratory personnel and the chemicals.
- Hood baffles or slots should be positioned properly. The top baffle/slot should be opened when chemicals with a vapor density of less than 1 (lighter than air) are used. The bottom baffle/slot should be opened when chemicals with vapor densities greater than 1 (heavier than air) are used.
- Chemicals and equipment (apparatus, instruments, etc.) should be placed at least 6 inches (15 cm) from the front edge of the hood.
- Equipment should be placed as far back in the hood as practical without blocking the baffles. Separate and elevate equipment by using blocks to ensure that air can flow easily around and under the equipment.
- Chemical fume hoods should be kept clean and free from unnecessary items and debris at all times. Solid material (paper, tissue, aluminum foil, etc.) should be kept from obstructing the rear baffles and from entering the exhaust ducts of the hood.
- Minimize the amount of bottles, beakers and equipment used and stored inside the hood because these items interfere with the airflow across the work surface of the hood.
- Chemicals should not be stored in a hood because they will likely become involved if there is an accidental spill, fire or explosion in the hood, thus creating a more serious problem.
- Sliding horizontal sash windows should not be removed from the hood sash.
- Laboratory personnel should not extend their head inside the hood when operations are in progress.

CHEMICAL FUME HOODS PROCEDURES FOR PROPER AND SAFE USE

(continued)

- The hood should not be used for waste disposal (evaporation).
- Hoods should be monitored daily by the user to ensure that air is moving into the hood. A strip of tissue taped to the hood sash will indicate if the hood is pulling air. Any hoods that are not working properly should be taken out of service and reported to the University Office of Environmental Health and Safety (855-6311). EH&S is responsible for inspecting chemical fume hoods annually.
- Perchloric acid must not be used in a regular chemical fume hood. Specially designed Perchloric Acid Fume Hoods must be utilized for this purpose. Call EH&S for more information.

CORROSIVE CHEMICALS PROCEDURES FOR SAFE HANDLING AND STORAGE

Corrosives (liquids, solids, and gases) are chemicals that cause visible destruction of, or irreversible alterations in, living tissue by chemical action at the site of contact. Corrosive effects can occur not only to the skin and eyes, but also to the respiratory tract through inhalation and to the gastrointestinal tract through ingestion. Corrosive liquids have a high potential to cause external injury to the body, while corrosive gases are readily absorbed into the body through skin contact and inhalation. Corrosive solids and their dusts can damage tissue by dissolving rapidly in moisture on the skin or within the respiratory tract when inhaled. In order to minimize these potential hazards, precautionary procedures must be observed when handling corrosives.

HANDLING

- Safety goggles, protective gloves, and a laboratory coat should always be worn when working with corrosive chemicals. A face shield, rubber apron, and rubber booties may also be appropriate depending on the work performed.
- Appropriate protective gloves that are resistant to permeation or penetration from corrosive chemicals should be selected and tested for the absence of pin holes prior to use.
- Eyewashes and safety showers should be readily available in areas where corrosive chemicals are used and stored. In the event of skin and eye contact with a corrosive chemical, the affected area should be immediately flushed with water for 15 minutes. Contaminated clothing should be removed and medical attention sought.
- Corrosive chemicals should be handled in a fume hood to ensure that any possible hazardous or noxious fumes generated are adequately vented.
- When mixing concentrated acids with water, add the acid slowly to the water. Allow the acid to run down the side of a container and mix slowly to avoid violent reactions and splattering. Never add water to acid.
- Appropriate spill material should be available in areas where corrosive chemicals are used and stored.
- Protective carriers should be used when transporting corrosive chemicals.

STORAGE

- Containers and equipment used for storage and processing of corrosive material should be corrosion resistant.
- Corrosive chemicals should be stored below eye level, preferably near the floor to minimize the danger of their falling from cabinets or shelves.
- Acids and caustics (i.e., bases) should be stored separately from each other. Secondary containers can be used to help with separation within a corrosive cabinet.
- Inorganic acids should be separated from organic acids and flammable/combustible material (inorganic acids are particularly reactive with flammable/combustible material).
- Acids should be segregated from active metals (e.g., sodium, potassium, and magnesium) and from chemicals that can generate toxic gases (e.g., sodium cyanide and iron sulfide).

FLAMMABLE AND COMBUSTIBLE LIQUIDS PROCEDURES FOR SAFE HANDLING AND STORAGE

Chemicals which exist, at ambient temperatures, in a liquid form with sufficient vapor pressure to ignite in the presence of an ignition source are called flammable or combustible liquids (note that the flammable/combustible liquid itself does not burn; it is the vapor from the liquid that burns). “**Flammables**” generate sufficient vapor at temperatures below 100 ° F (37.8 °C), whereas “**Combustibles**” generate sufficient vapor at temperatures at or above 100 °F. Invisible vapor trails from these liquids can reach remote ignition sources causing flashback fires. In addition, these liquids become increasingly hazardous at elevated temperatures due to more rapid vaporization. For these reasons, precautionary measures must be observed when handling and storing flammables and combustibles.

CLASSIFICATION

<u>Classification</u>	<u>Flash Point</u> ¹	<u>Boiling Point</u>
Flammable Liquid		
Class IA	<73 ° F (22.8 °C)	< 100 °F (37.8 °C)
Class IB	<73 ° F	≥100 °F
Class IC	≥73 ° F and <100 °F	-----
Combustible Liquid		
Class II	≥100 °F and < 140 °F (60 °C)	-----
Class IIIA	≥140 °F and < 200 °F (93 °C)	-----

¹The minimum temperature at which a liquid gives off vapor in sufficient concentration to form an ignitable mixture in air near the surface of a liquid.

HANDLING

- Appropriate personal protective equipment (gloves, lab coat, and safety goggles) should be worn when working with flammable/combustible liquids.
- Flammable/combustible liquids should never be heated using open flames. Preferred heat sources include steam baths, water baths, oil baths, hot air baths, and heating mantels.
- Ignition sources should be eliminated in areas where flammable vapors may be present.
- Flammable/combustible liquids should only be dispensed under a fume hood. Ventilation is one of the most effective ways to prevent the formation and concentration of flammable vapors.
- When pouring from containers of 1 gallon (3.8 liters) or greater capacity, make sure both containers involved are electrically interconnected by bonding to each other and to a ground. The friction of flowing liquid may be sufficient to generate static electricity, which in turn may discharge, causing a spark and ignition.

FLAMMABLE AND COMBUSTIBLE LIQUIDS PROCEDURES FOR SAFE HANDLING AND STORAGE

(continued)

- Flammable/combustible liquids in containers larger than 1 gallon (3.8 liters) should be transferred to smaller containers that can be easily manipulated by one person.
- Appropriate fire extinguishers should be available in areas where flammables are used.

STORAGE

- Flammable/combustible liquid in quantities exceeding a total of 10 gallons (38 liters) within a laboratory should be stored in approved flammable storage cabinets or safety cans.
- Flammable/combustible liquid stored outside of flammable storage cabinets in the laboratory should be kept to the minimum necessary for the work being done.
- Containers larger than 5 gallons (19 liters) shall not be stored in the laboratory.
- Flammable/combustible liquid stored in glass containers shall not exceed 1 gallon (3.8 liters).
- Flammable storage cabinets and safety cans should not be altered or modified unless specified by Indiana's Fire Prevention Code/National Fire Protection Agency guidelines.
- Flammable/combustible liquids should only be stored in explosion-proof or laboratory-safe refrigeration equipment.
- Flammable/combustible liquid containers filled or empty should not be stored in hallways or obstructing exits.
- Waste flammable/combustible liquids should be stored in safety cans.
- Flammables and combustibles should not be stored near oxidizers, corrosives, combustible material, or near heat sources. Make sure all chemicals stored near flammable and combustibles are compatible.

OXIDIZING AGENTS PROCEDURES FOR SAFE HANDLING AND STORAGE

Oxidizing agents are chemicals that bring about an oxidation reaction. The oxidizing agent may 1) provide oxygen to the substance being oxidized (in which case the agent has to be oxygen or contain oxygen) or 2) receive electrons being transferred from the substance undergoing oxidation (chlorine is a good oxidizing agent for electron-transfer purposes, even though it does not contain oxygen). The intensity of the oxidation reaction depends on the oxidizing-reducing potential of the material involved. Fire or explosion is possible when strong oxidizing agents come into contact with easily oxidizable compounds, such as metals, metal hydrides or organics. Because oxidizing agents possess varying degrees of instability, they can be explosively unpredictable.

EXAMPLES OF OXIDIZING AGENTS

Gases: fluorine, chlorine, ozone, nitrous oxide, oxygen

Liquids: hydrogen peroxide, nitric acid, perchloric acid, bromine, sulfuric acid

Solids: nitrites, nitrates, perchlorates, peroxides, chromates, dichromates, picrates, permanganates, hypochlorites, bromates, iodates, chlorites, chlorates, persulfates

HANDLING

- Appropriate personal protective equipment (safety goggles, gloves, lab coat, etc.) should be worn when working with oxidizers.
- If a reaction is potentially explosive, or if the reaction is unknown, use a fume hood (with the sash down as a protective barrier), safety shield, or other methods for isolating the material or the process.
- Oxidizers can react violently when in contact with incompatible materials. For this reason, know the reactivity of the material involved in an experimental process. Assure that no extraneous material is in the area where it can become involved in a reaction.
- The quantity of oxidizer used should be the minimum necessary for the procedure. Do not leave excessive amounts of an oxidizer in the vicinity of the process.
- Perchloric acid must not be used in a regular chemical fume hood. A specially designed Perchloric Acid Fume Hood must be utilized for this purpose. Contact EH&S (855-6311) for more information.

STORAGE

- Oxidizers should be stored in a cool, dry place.
- Oxidizers should be segregated from organic material, flammables, combustibles and strong reducing agents such as zinc, alkaline metals, and formic acid.
- Oxidizing acids such as perchloric acid and nitric acid should be stored separately in compatible secondary containers away from other acids.

For the purpose of storage, the Uniform and International Building Code and the National Fire Protection Association classify oxidizers based on the increase in the burning rate of the combustible material with which it comes into contact. See Appendix C for the definitions and a list of examples. Contact EH&S (855-6311) for more information.

REACTIVE CHEMICALS PROCEDURES FOR SAFE HANDLING AND STORAGE

Reactives are substances that have the potential to vigorously polymerize, decompose, condense, or become self-reactive due to shock, pressure, temperature, light, or contact with another material. All reactive hazards involve the release of energy in a quantity or at a rate too great to be dissipated by the immediate environment of the reaction system, so that destructive effects occur. Reactive chemicals include: 1) **explosives**, 2) **organic peroxides**, 3) **water-reactives** and 4) **pyrophorics**. Effective control is essential to minimize the occurrence of reactive chemical hazards.

- 1) **EXPLOSIVES** - cause sudden, almost instantaneous release of pressure, gas, and heat when subjected to sudden adverse conditions. Heat, light, mechanical shock, detonation, and certain catalysts can initiate explosive reactions. Compounds containing the functional groups azide, acetylide, diazo, nitroso, haloamine, peroxide, and ozonide are sensitive to shock and heat and can explode violently.
 - Appropriate personal protective equipment (face shield, safety goggles, leather outer gloves, chemical resistant gloves, lab coat, etc.) should be worn when working with explosives.
 - Before working with explosives, understand their chemical properties, know the products of side reactions, the incompatibility of certain chemicals, and monitor environmental catalysts such as temperature changes.
 - Containers should be dated upon receipt and when opened. Expired explosives should be discarded promptly.
 - Explosives should be kept to the minimum necessary for the procedure.
 - If there is a chance of explosion, use protective barriers (e.g., fume hood sash and safety shield) or other methods for isolating the material or process.
 - Explosives should be stored in a cool, dry, and protected area. Segregate from other material that could create a serious risk to life or property should an accident occur.

- 2) **ORGANIC PEROXIDES** - contain an -O-O- structure bonded to organic groups. These compounds can be considered as structural derivatives of hydrogen peroxide, H-O-O-H, in which one or both of the hydrogen atoms have been replaced by an organic group. Generally, organic peroxides are low-powered explosives that are sensitive to shock, sparks, and heat due to the weak -O-O- bond which can be cleaved easily. Some organic compounds such as ethers, tetrahydrofuran, and p-dioxane can react with oxygen from the air forming unstable peroxides. Peroxide formation can occur under normal storage conditions, when compounds become concentrated by evaporation, or when mixed with other compounds. These accumulated peroxides can violently explode when exposed to shock, friction, or heat.
 - Appropriate personal protective equipment (safety goggles, gloves, lab coat, etc.) should be worn when working with organic peroxides or peroxide-forming compounds.
 - Containers should be labeled with the receiving and opening dates. Unopened material should be discarded within 1 year and opened material should be discarded within 6 months.

REACTIVE CHEMICALS PROCEDURES FOR SAFE HANDLING AND STORAGE

(continued)

- Containers should be airtight and stored in a cool, dry place away from direct sunlight. Segregate from incompatible chemicals.
 - Peroxide formers, liquid peroxides, or solutions should not be refrigerated below the temperature at which the peroxide freezes or precipitates. Peroxides in these forms are extra sensitive to shock (never store diethyl ether in a refrigerator or freezer).
 - Unused peroxides should never be returned to the stock container.
 - Metal spatulas should not be used with peroxide formers. Only ceramic or plastic spatulas should be used. Contamination by metal can cause explosive decomposition.
 - Friction, grinding, and all forms of impact, especially with solid organic peroxides should be avoided. Never use glass containers with screw cap lids or glass stoppers. Instead, use plastic bottles and sealers.
 - Testing for the presence of peroxides should be performed periodically.
 - Containers with obvious crystal formation around the lid or viscous liquid at the bottom of the container should NOT be opened or moved. Call EH&S at 855-6311 for disposal.
- 3) **WATER-REACTIVES** - react with water or moisture in the air releasing heat or flammable, toxic gas. Examples include alkali metals, alkaline earth metals, carbides, hydrides, inorganic chlorides, nitrides, peroxides, and phosphides.
- Appropriate personal protective equipment (safety goggles, gloves, lab coat, etc.) should be worn when working with water-reactives.
 - Water-reactives should be stored under mineral oil in a cool, dry place. Isolate from other chemicals.
 - Water-reactives should not be stored near water, alcohols, and other compounds containing acidic OH.
 - In case of fire, keep water away. Appropriate fire extinguishers should be available in areas where water-reactives are used (use a Type “D” fire extinguisher to extinguish active metal fires).
- 4) **PYROPHORICS** - ignite spontaneously in air below 130 °F (54 °C). Often the flame is invisible. Examples of pyrophoric materials include silane, silicon tetrachloride, white and yellow phosphorus, sodium, tetraethyl lead, potassium, nickel carbonyl, and cesium.
- Appropriate personal protective equipment (safety goggles, gloves, lab coat, etc.) should be worn when working with pyrophorics.
 - Pyrophorics should be used and stored in inert environments.
 - Appropriate fire extinguishers should be available in areas where pyrophorics are used.

CARCINOGENS, REPRODUCTIVE TOXINS, AND ACUTELY TOXIC CHEMICALS PROCEDURES FOR SAFE HANDLING AND STORAGE

The Occupational Safety and Health Administration (OSHA) Laboratory Standard requires that special handling procedures be employed for certain chemicals identified as "particularly hazardous substances." Particularly hazardous substances include chemicals that are "select" carcinogens, reproductive toxins, and chemicals that have a high degree of acute toxicity. In addition, many chemicals used (including novel chemicals that are synthesized) in research laboratories have not been tested explicitly for carcinogenic or toxic properties and should therefore be handled as "particularly hazardous substances" since their hazards are unknown.

Carcinogen - substance that either causes cancer in humans, or because it causes cancer in animals, is considered capable of causing cancer in humans. OSHA defines those substances that are known to pose the greatest carcinogenic hazards as "select" carcinogens (see Appendix C). These materials include substances that:

1. OSHA regulates as a carcinogen; or
2. The National Toxicology Program (NTP) lists as "known to be a carcinogen" or "reasonably anticipated to be a carcinogen" in their Annual Report on Carcinogens; or
3. The International Agency for Research on Cancer (IARC) lists under Group 1 ("carcinogenic to humans"), Group 2A ("probably carcinogenic to humans"), or Group 2B ("possibly carcinogenic to humans").

Reproductive/Developmental Toxin - substance that cause chromosomal damage or genetic alterations (mutagens) or substances with lethal or teratogenic (malformations or physical defects) in a developing fetus or embryo.

Acutely Toxic Chemicals - Acute toxicity is the ability of a chemical to cause a harmful effect after a single exposure. Acutely toxic chemicals can cause local toxic effects, systemic effects, or both. In general, acutely toxic chemicals have an Oral LD50 of < 50 mg (rats, per kg), Skin Contact LD50 of < 200 mg (rabbits, per kg), Inhalation LC50 of <200 (rats, ppm for 1 hr) OR <2000 (rats, mg/m³ for 1 hr).

HANDLING

- Designated areas (e.g., fume hoods, glove boxes, lab benches, outside rooms, etc.) for material use should be established and the areas identified by signs or postings.
- Containment devices such as fume hoods (if necessary) and personal protective equipment (gloves, lab coat, and eye protection) should be used when handling these hazardous substances.
- Procedures for the safe use of the material and waste removal should be established prior to use.
- Decontamination procedures should be developed in advance and strictly followed.

**CARCINOGENS, REPRODUCTIVE TOXINS,
AND ACUTELY TOXIC CHEMICALS
PROCEDURES FOR SAFE HANDLING AND STORAGE**

(continued)

- Only laboratory personnel trained to work with these substances should perform the work, and always within the designated area. Prior approval is required by the principal investigator or supervisor (see Section 2.1.1 *Prior Approval of Hazardous Operations*).
- Only the minimum quantity of the material should be used.

STORAGE

- These materials should be stored in areas designated for “particularly hazardous substances.”
- Storage areas should be clearly marked with the appropriate hazard warning signs.
- All containers of these materials (even if the material is in very small quantities such as 0.1%) should be clearly labeled with the chemical name or mixture components and the appropriate hazard warning information.
- Chemical storage areas should be secure to avoid spills or broken containers.
- Storage areas or laboratory rooms should be locked when laboratory personnel are gone.

COMPRESSED GASES PROCEDURES FOR SAFE HANDLING AND STORAGE

In general, a compressed gas is any material contained under pressure that is dissolved or liquefied by compression or refrigeration. Compressed gas cylinders should be handled as high-energy sources and therefore as potential explosives and projectiles. Prudent safety practices should be followed when handling compressed gases since they expose workers to both chemical and physical hazards.

HANDLING

- Safety glasses with side shields (or safety goggles) and other appropriate personal protective equipment should be worn when working with compressed gases.
- Cylinders should be marked with a label that clearly identifies the contents.
- All cylinders should be checked for damage prior to use. Do not repair damaged cylinders or valves. Damaged or defective cylinders, valves, etc., should be taken out of use immediately and returned to the manufacturer/distributor for repair.
- All gas cylinders (full or empty) should be rigidly secured to a substantial structure at 2/3 height. Only two cylinders per restraint are allowed in the laboratory and only soldered link chains or belts with buckles are acceptable. Cylinder stands are also acceptable but not preferred.
- Handcarts shall be used when moving gas cylinders. Cylinders must be chained to the carts.
- All cylinders must be fitted with safety valve covers before they are moved.
- Only three-wheeled or four-wheeled carts should be used to move cylinders.
- A pressure-regulating device shall be used at all times to control the flow of gas from the cylinder.
- The main cylinder valve shall be the only means by which gas flow is to be shut off. The correct position for the main valve is all the way on or all the way off.
- Cylinder valves should never be lubricated, modified, forced, or tampered.
- After connecting a cylinder, check for leaks at connections. Periodically check for leaks while the cylinder is in use.
- Regulators and valves should be tightened firmly with the proper size wrench. Do not use adjustable wrenches or pliers because they may damage the nuts.
- Cylinders should not be placed near heat or where they can become part of an electrical circuit.
- Cylinders should not be exposed to temperatures above 50 °C (122 °F). Some rupture devices on cylinders will release at about 65 °C (149 °F). Some small cylinders, such as lecture bottles, are not fitted with rupture devices and may explode if exposed to high temperatures.
- Rapid release of a compressed gas should be avoided because it will cause an unsecured gas hose to whip dangerously and also may build up enough static charge to ignite a flammable gas.
- Appropriate regulators should be used on each gas cylinder. Threads and the configuration of valve outlets are different for each family of gases to avoid improper use. Adaptors and homemade modifications are prohibited.
- Cylinders should never be bled completely empty. Leave a slight pressure to keep contaminants out.

COMPRESSED GASES PROCEDURES FOR SAFE HANDLING AND STORAGE

(continued)

STORAGE

- When not in use cylinders should be stored with their main valve closed and the valve safety cap in place.
- Cylinders must be stored upright and not on their side. All cylinders should be secured.
- Cylinders awaiting use should be stored according to their hazard classes.
- Cylinders should not be located where objects may strike or fall on them.
- Cylinders should not be stored in damp areas or near salt, corrosive chemicals, chemical vapors, heat, or direct sunlight. Cylinders stored outside should be protected from the weather.

SPECIAL PRECAUTIONS

Flammable Gases

- No more than two cylinders should be manifolded together; however several instruments or outlets are permitted for a single cylinder.
- Valves on flammable gas cylinders should be shut off when the laboratory is unattended and no experimental process is in progress.
- Flammable gas cylinders should be grounded. (Do not ground to an electrical outlet.)
- Flames involving a highly flammable gas should not be extinguished until the source of the gas has been safely shut off; otherwise it can reignite causing an explosion.

Acetylene Gas Cylinders

- Acetylene cylinders must always be stored upright. They contain acetone, which can discharge instead of or along with acetylene. Do not use an acetylene cylinder that has been stored or handled in a nonupright position until it has remained in an upright position for at least 30 minutes.
- The outlet line of an acetylene cylinder must be protected by a flame arrestor.
- Compatible tubing should be used to transport gaseous acetylene. Some tubing like copper forms explosive acetylides.

Lecture Bottles

- All lecture bottles should be marked with a label that clearly identifies the contents.
- Lecture bottles should be stored according to their hazard classes.
- Lecture bottles, which contain toxic gases, should be stored in a ventilated cabinet.
- Lecture bottles should be stored in a secure place to eliminate them from rolling or falling.
- Lecture bottles should not be stored near corrosives, heat, direct sunlight, or in damp areas.
- To avoid costly disposal fees, lecture bottles should only be purchased from suppliers that will accept returned bottles (full or empty). Contact the supplier before purchasing lecture bottles to ensure that they have a return policy.
- Lecture bottles should be dated upon initial use. It is advised that bottles be sent back to the supplier after one year to avoid accumulation of old bottles.

CRYOGENIC LIQUIDS PROCEDURES FOR SAFE HANDLING AND STORAGE

Cryogenic liquids are liquefied gases having boiling points of less than $-73.3\text{ }^{\circ}\text{C}$ ($-100\text{ }^{\circ}\text{F}$). The primary hazards of cryogenic liquids include both physical hazards such as fire, explosion, and pressure buildup and health hazards such as severe frostbite and asphyxiation. Potential fire or explosion hazards exist because cryogenic liquids are capable, under the right conditions, of condensing oxygen from the atmosphere. This oxygen-rich environment in combination with flammable/combustible materials, and an ignition source are particularly hazardous. Pressure is also a hazard because of the large volume expansion ratio from liquid to gas that a cryogen exhibits as it warms and the liquid evaporates. This expansion ratio also makes cryogenic liquids more prone to splash and therefore skin and eye contact is more likely to occur. Contact with living tissue can cause frostbite or thermal burns, and prolonged contact can cause blood clots that have very serious consequences. All laboratory personnel should follow prudent safety practices when handling and storing cryogenic liquids.

PROPERTIES OF COMMON CRYOGENIC LIQUIDS

<u>Gas</u>	<u>Boiling Point ($^{\circ}\text{C}$)</u>	<u>Volume Expansion Ratio</u>
Helium	-269	757-1
Hydrogen	-252.7	851-1
Nitrogen	-195.8	696-1
Fluorine	-187.0	888-1
Argon	-185.7	847-1
Oxygen	-183.0	860-1
Methane	-161.4	578-1

HANDLING

- Appropriate personal protective equipment should be worn when handling cryogenic liquids. This includes special cryogen gloves, safety goggles, full face shield, impervious apron or coat, long pants, and high topped shoes. Gloves should be impervious and sufficiently large to be readily removed should a cryogen be spilled. Watches, rings, and other jewelry should NOT be worn.
- Unprotected body parts should not come in contact with vessels or pipes that contain cryogenic liquids because extremely cold material may bond firmly to the skin and tear flesh if separation is attempted.
- Objects that are in contact with cryogenic liquid should be handled with tongs or proper gloves.
- All precautions should be taken to keep liquid oxygen from organic materials; spills on oxidizable surfaces can be hazardous.
- All equipment should be kept clean, especially when working with liquid or gaseous oxygen.
- Work areas should be well ventilated.
- Transfers or pouring of cryogenic liquid should be done very slowly to minimize boiling and splashing.

CRYOGENIC LIQUIDS
PROCEDURES FOR SAFE HANDLING AND STORAGE
(continued)

- Cryogenic liquids and dry ice used as refrigerant baths should be open to the atmosphere. They should never be in a closed system where they may develop uncontrolled or dangerously high pressure.
- Liquid hydrogen should not be transferred in an air atmosphere because oxygen from the air can condense in the liquid hydrogen presenting a possible explosion risk.

STORAGE

- Cryogenic liquids should be handled and stored in containers that are designed for the pressure and temperature to which they may be subjected. The most common container for cryogenic liquids is a double-walled, evacuated container known as a dewar flask.
- Containers and systems containing cryogenic liquids should have pressure relief mechanisms.
- Cylinders and other pressure vessels such as dewar flasks used for the storage of cryogenic liquids should not be filled more than 80% of capacity, to protect against possible thermal expansion of the contents and bursting of the vessel by hydrostatic pressure. If the possibility exists that the temperature of the cylinder may increase to above 30 °C (86 °F), a lower percentage (i.e., 60 percent capacity) should be the limit.
- Dewar flasks should be shielded with tape or wire mesh to minimize flying glass and fragments should an implosion occur.
- Dewar flasks should be labeled with the full cryogenic liquid name and hazard warning information.

ELECTRICAL SAFETY PROCEDURES

Serious injury or death by electrocution is possible when appropriate attention is not given to the engineering and maintenance of electrical equipment and personal work practices around such equipment. In addition, equipment malfunctions can lead to electrical fires. By taking reasonable precautions, electrical hazards in the laboratory can be dramatically minimized.

- Laboratory personnel should know the location of electrical shut-off switches and/or circuit breakers in or near the laboratory so that power can be quickly terminated in the event of a fire or accident.
- Electrical panels and switches should never be obstructed and should be clearly labeled to indicate what equipment or power source they control.
- All electrical equipment should be periodically inspected to ensure that cords and plugs are in good condition. Frayed wires and wires with eroded or cracked insulation should be repaired immediately, especially on electrical equipment located in wet areas such as cold rooms or near cooling baths. Insulation on wires can easily be eroded by corrosive chemicals and organic solvents.
- All electrical outlets should have a grounding connection requiring a three-pronged plug.
- All electrical equipment should have three-pronged, grounded connectors. The only exception to this rule are instruments entirely encased in plastic (such as electric pipettors and some types of microscopes) and Glas-Col heating mantels. If equipment does not have a three-pronged plug, replace the plug and cord to ground the equipment.
- Face plates must not be removed from electrical outlets.
- Electrical wires should not be used as supports.
- Extension cords should be avoided. If used, they should have three-pronged, grounded connectors and positioned or secured as not to create a tripping hazard.
- All shocks should be reported to the principal investigator or supervisor. All faulty electrical equipment should be immediately removed from service until repaired.
- Electrical outlets, wiring, and equipment within a laboratory or building should only be repaired by IU Physical Plant or other professional electricians.
- Proper grounding and bonding of flammable liquid containers should be practiced to avoid the build-up of excess static electricity. Sparks generated from static electricity are good ignition sources.

GLASSWARE AND SHARPS PROCEDURES FOR SAFE HANDLING AND DISPOSAL

HANDLING

- Glassware should be handled and stored carefully to avoid damage.
- Chipped, broken, or star-cracked glassware should be discarded or repaired. Damaged glassware should never be used.
- Only thick-walled, pressure resistant glassware should be utilized under a vacuum.
- Appropriate hand protection should be used when picking up broken glass or other sharp objects. Small pieces should be swept up using a brush and dustpan.
- Appropriate hand protection should be used when inserting glass tubing into a rubber stopper or when placing rubber tubing on glass hose connections. Use of plastic or metal connectors should be considered.

DISPOSAL

- All broken glassware that cannot be repaired should be rinsed thoroughly and collected in a suitable-sized, hard plastic receptacle labeled “BROKEN GLASSWARE.” The custodial staff will discard the contents of these containers.
- All sharps (needles, razors, etc), regardless of contamination, should be placed in puncture resistant cardboard boxes or plastic containers, except for broken glassware as stated above.
- Sharps and glassware that are contaminated with chemicals should be collected in puncture-resistant containers and labeled as “Sharps” and “CCI” (Chemically Contaminated Items). Sharps should be picked up by EH&S by appointment or delivered to Open House for disposal.
- All sharps and glassware contaminated with biological materials must be discarded according to the procedures outlined in the *Biohazardous Waste Disposal* policy found in the *Hazardous Waste Disposal Guide*. Sharps containers are sold in chemistry stores, the biology stock room and laboratory supply catalogues.

*Note: **Red** biohazard sharps containers are to be used **only** for biohazardous waste. Regulatory requirements prohibit disposal by the same means as chemically contaminated sharps.*

- All sharps and glassware contaminated with radioactive materials must be discarded according to procedures outlined in Indiana University’s *Radiation Safety Manual*.

CHEMICAL SPILL RESPONSE PROCEDURES

Despite the best effort of researchers to practice safe science in the laboratory, accidents resulting in the release of chemicals will occur. For this reason, it is essential that laboratory personnel have a spill response plan that includes appropriate procedures and materials to adequately contain and cleanup a spill. The following procedures should be used as a guide to help laboratory personnel design an effective spill control plan for their laboratory (see Section 6.10 *Spill Control Kit* for information on spill kit contents). For more detailed information on spills that require special attention and handling (e.g., acid chlorides, mercury, alkali metals, white and yellow phosphorus, bromine, and hydrofluoric acid refer to EH&S's *Chemical Spill Response Guide*.

Spill Response - Major Spill

In the event of a spill which: 1) involves the release of a type or quantity of chemical which poses an immediate risk to health; 2) involves an uncontrolled fire or explosion; or 3) involves serious personal injury; follow the steps outlined in the *Emergency Information* section at the beginning of this Plan.

Spill Response - Minor Spill

In the event of a spill involving the release of a type or quantity of chemical that does not pose an immediate risk to health:

1. Notify other laboratory personnel of the accident.
2. Isolate the area. Close laboratory doors and evacuate the immediate area if necessary.
3. Remove all ignition sources and establish exhaust ventilation. Vent vapors to outside of building only (open windows and turn on fume hood).
4. Choose appropriate personal protective equipment (goggles, face shield, impervious gloves, lab coat, apron or coveralls, boots, respirator, etc.) (All laboratory personnel must be properly fit tested before using a respirator). Contact EH&S for more information.
5. Confine and contain the spill. Cover with appropriate absorbent material. Sweep solid material into a dust pan and place in a sealed plastic container. Decontaminate the area with soap and water after cleanup and place residue in a plastic bag or another sealed plastic container. Bring the containers to EH&S's Open House or call EH&S for pickup.

**FOR CONSULTATION OR ASSISTANCE CALL
ENVIRONMENTAL HEALTH AND SAFETY:**

**855-6311
(8a.m.-5p.m., Mon.-Fri.)**

GLASS APPARATUS AND PLASTICWARE ASSEMBLY

Borosilicate glassware is recommended for all laboratory glassware except for special experiments that use ultra violet (UV) or other light sources. The only soft glass provided in the laboratory should be reagent bottles, measuring equipment, stirring rods, and tubing.

Any glass equipment to be evacuated, such as suction flasks, should be specially designed with heavy walls. Dewar flasks and large vacuum vessels should be taped or otherwise screened or contained in a metal jacket to prevent flying glass in the case of an implosion. Household Thermos bottles have thin walls and are not acceptable substitutes for laboratory Dewar flasks.

PREPARATION OF GLASS TUBING AND STOPPERS

To cut glass tubing:

- Hold the tubing against a firm support and make one quick firm stroke with a sharp triangular file or glass cutter long enough to extend approximately one-third round the circumference.
- Cover the tubing with cloth and hold the tubing in both hands, away from the body.
- Place the thumbs on the tubing opposite the nick 2 to 3 cm (1 in.) apart and extended toward each other.
- Push out on the tubing with the thumbs as you pull the sections apart, but do not deliberately bend the glass with the hands.

If the tubing does not readily pull apart, the nick probably is too shallow or rounded, make a fresh sharp file scratch in the same place and repeat the operation. Avoid accidental contact of the tubing with a nearby person by standing with your back toward a wall or lab bench.

All glass tubing and rods, including stirring rods, should be fire polished before use. Unpolished cut glass has a razor-like edge, which not only can lacerate the skin, but will also cut into a stopper or rubber hose, making it difficult to insert the glass properly; After polishing or bending glass, allow ample time for it to cool before grasping it.

To drill a stopper:

- Use only a sharp borer one size smaller than that which will just slip over the glass tube.
- Lubricate rubber stoppers with water or glycerol.
- Bore the hole by slicing through the stopper, twisting with moderate forward pressure, grasping the stopper only with the fingers, and keeping the hand away from the back of the stopper.
- Keep the index finger of the drilling hand against the barrel of the borer and close to the stopper to stop the borer when it breaks through.
- It is preferable to drill only part way through and then finish by drilling from the opposite side. Discard a stopper if a hole is irregular or does not fit the inserted tube snugly, if it is cracked, or if it leaks.
- Corks should have been previously softened by rolling and kneading. Rubber or cork stoppers should fit into a joint so that one-third to one-half of the stopper is inserted.

GLASS APPARATUS AND PLASTICWARE ASSEMBLY

(continued)

When available, glassware with ground joints is preferable. Glass stoppers and joints should be clean, dry and lightly lubricated.

INSERTION OF GLASS TUBES OR RODS INTO STOPPERS OR FLEXIBLE TUBING

To insert glass tubes into stoppers or flexible tubing:

- Make sure the diameter of the tube or rod is compatible with the diameter of the hose or stopper.
- If not already fire polished, fire polish the end of the glass to be inserted; let it cool.
- Lubricate the glass. Water may be sufficient but glycerol is a better lubricant.
- Wear heavy gloves or wrap layers of cloth around the glass and protect the other hand by holding the hose or stopper with a layered cloth pad.
- Hold the glass rod or tube near the end to be inserted, not more than 5 cm (2 in) from the end.
- Insert the glass with a slight twisting motion, avoiding too much pressure and torque.
- If necessary, use a cork borer as a sleeve for insertion of glass tubes.
- Substitute a piece of metal tubing for glass tubing if possible.
- Remove stuck tubes by slitting the hose or stopper with a sharp knife.

APPARATUS ASSEMBLY

The following recommendations will help make apparatus assembly easier, safer, and avoid equipment failure during use:

- Keep your workspace free of clutter.
- Set up clean, dry apparatus, firmly clamped and well back from the edge of the lab bench or hood with due regard to the proximity of reagent bottles to burners and to other workers and their equipment. Choose sizes that can properly accommodate the operation to be performed, allowing 20% free space at the minimum.
- Use only equipment that is free from flaws such as cracks, chips, frayed wire, and obvious defects. Glassware can be examined in polarized light for stains. Even the smallest chip or crack renders glassware unusable; chipped or cracked ware should be repaired or discarded.
- A properly placed pan under a reaction vessel or container will act as a secondary containment to confine spilled liquids in the event of glass breakage.
- Addition and separatory funnels should be properly supported and oriented so that the stopcock will not be loosened by gravity. A retainer ring should be used on the stopcock plug. Glass stopcocks should be freshly lubricated. Teflon stopcocks should not need lubrication.
- Condensers should be properly supported with securely positioned clamps. The attached water hoses must be secured to the glass fittings with wire or appropriate hose clamps.

GLASS APPARATUS AND PLASTICWARE ASSEMBLY

(continued)

Stirrer motors and vessels should be secured to maintain proper alignment. Magnetic stirring is preferable.

- Apparatus attached to a ring stand should be positioned so that the center of gravity of the system is over the base and not to one side. There should be adequate provision for removing burners or baths quickly. Standards bearing heavy loads should be firmly attached to the bench top. Equipment racks should be securely anchored at the top and bottom.

OPERATIONAL PRECAUTIONS

The following precautions should be considered prior to assembly and during operation of the apparatus.

- When working with flammable gases or liquids, do not allow burners or other ignition sources in the vicinity. Use appropriate traps, condensers, or scrubbers to minimize release of vapors to the environment. If a hot plate is used, ensure that the temperatures of all exposed surfaces are less than the autoignition temperature of the chemicals likely to be released and that the temperature control device and the stirring or ventilating motors do not spark
- Only non-sparking motors or pneumatic motors should be used in chemical laboratories.
- Whenever possible, use controlled electrical heaters or steam in place of gas burners.
- Inspect power cords for chemical or physical damage by unplugging the equipment then bend the cord to look for cracks in the insulation. Be sure to check carefully and close to the point where the power cord enters the housing.
- Apparatus, equipment, or chemical bottles should not be placed on the floor.
- Never heat a closed container. Provide a vent as part of the apparatus for chemicals that are to be heated. Prior to heating a liquid, place boiling stones in unstirred vessels (except test tubes). If a burner is to be used, distribute the heat with a ceramic-centered wire gauze. Use a thermometer with its bulb in the boiling liquid if there is the possibility of a dangerous exothermic decomposition as in some distillations. This will provide a warning and may allow time to remove the heat and apply external cooling. The setup should allow for fast removal of heat.
- Whenever hazardous gases or fumes are likely to be evolved, an appropriate gas trap should be used and the operation confined to a fume hood.
- Fume hoods are recommended for all operations in which toxic or flammable vapors are evolved as in many distillations. Most vapors have a density greater than that of air and will settle on a bench top or floor where they may diffuse to a distant burner or ignition source. These vapors will roll out over astonishingly long distances and, if flammable, an ignition can cause a flash back to the source of the vapors. Once diluted with significant amounts of air, vapors move in air essentially as air itself.
- Use a hood when working with a system under reduced pressure (which may implode). Close the sash to provide a shield. If a hood is not available, use a standing shield. Shields that can be knocked over must be stabilized with weights or fasteners. Standing shields are preferably secured near the top. Proper eye and face protection must be worn even when using the shields or hood.

SOLVENT STILLS PROCEDURES FOR SET-UP, USE, AND NEUTRALIZATION

Although the procedures for purifying laboratory chemicals are inherently safe, care must be exercised if hazards are to be avoided. Solvent distillation equipment in which flammable liquids are purified by distillation with reactive metals or metal hydrides such as Na, K, CaH₂, or LiAlH₄ are possibly the greatest danger in any organic chemistry laboratory. The potential fire and explosion hazards associated with the combination of air- and/or water-reactive metals with large amounts of organic solvents are great and the effects on personnel and equipment can be catastrophic. The chances of personnel escaping such an incident unharmed are very low. **Consider using alternative solvent purification systems and methods before proceeding. (See column purification method below for a procedure that avoids all heat and distillation.)**

SET-UP AND OPERATION

1. Use proper personal protective equipment (gloves, safety glasses, and lab coat) while operating a distillation unit.
2. Any solvent stills containing reactive metals should be located in a fume-hood.
3. After set up and before start up get prior approval and a final equipment check from the principal investigator or an approved competent person.
4. The total volume of solvent used in these stills shall be kept to a minimum [BUT they should never be allowed to go “dry”.] Their useful working volume is ¼ to 2/3 of filled capacity.
5. Stills should be operated under an inert gas atmosphere of nitrogen or argon.
6. Several types of drying agents can be used:
 - a) Na, K, or Na/K must never be used for solvents containing C-Cl or O-H bonds.
 - b) Because of their pyrophoric nature (possible spontaneous ignition upon contact with air) the use of sodium/potassium alloys (NaK), which are liquids at ambient temperature should be avoided. Solvent flasks containing LiAlH₄ must never be heated. As a drying agent LiAlH₄ is therefore only suitable for non-reducible solvents that can be obtained pure by flask-to-flask vacuum-transfer at ambient temperature.
 - c) The use of potassium alone is recommended for THF only – in these solvents the metal will melt providing a fresh & reactive surface. Be aware that it is much more reactive than sodium, especially when quenching a solvent still (see below).
 - d) The use of sodium alone is recommended for diethyl ether and all other hydrocarbons such as toluene, benzene, pentane, hexane, heptane, etc.
 - e) Calcium hydride is recommended for methylene chloride and other halogenated solvents.
 - f) Magnesium/Iodine is recommended for methanol and ethanol.
 - g) For all high boiling solvents the use of 4 Å molecular sieves (activated by heating under full dynamic vacuum overnight) is recommended.

SOLVENT STILLS

PROCEDURES FOR SET-UP, USE, AND NEUTRALIZATION

(continued)

7. Solvent stills should never be left running (i.e., being heated to reflux) while unattended – especially not overnight.
8. Stills should be deactivated and restarted with all fresh solvent and drying agents on a regular basis to avoid buildup of metal hydroxides and benzophenone “cakes” that would impair stirring necessary during deactivation.
9. To deactivate a solvent still containing reactive metals follow the procedure below for deactivation and neutralization.

Reference: Armarego, W.L.F., Perrin, D.D., *Purification of Laboratory Chemicals*, Fourth Edition, 1998.

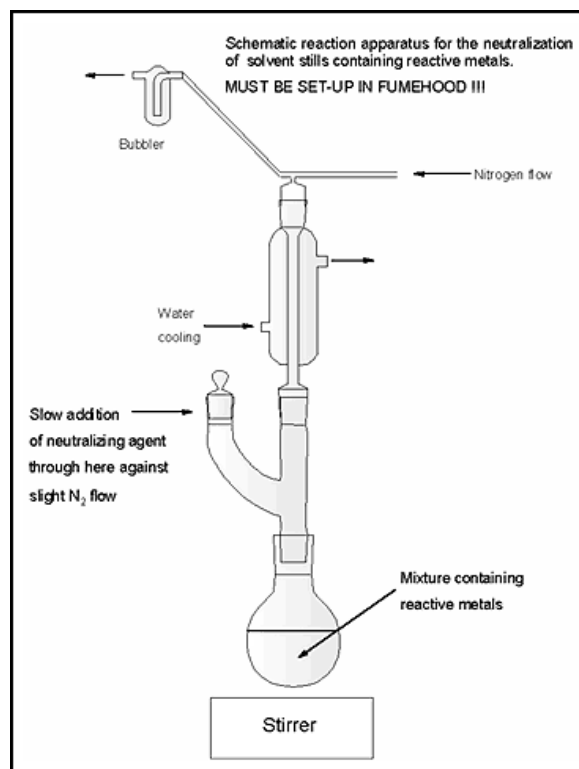
DEACTIVATION AND NEUTRALIZATION

Please read and follow these procedures carefully. **This procedure can be dangerous** and requires plenty of time to complete. Do not rush the process. Only properly trained persons are to perform this procedure.

1. Notify other laboratory occupants and your supervisor of your intent to perform this procedure. Do not perform this procedure "after-hours".
2. Wear a lab coat, safety glasses, face shield, and gloves. Orient yourself with the location of the nearest emergency shower, fire blanket, and exit. Have a dry-chemical fire extinguisher available.
3. Inspect the still flask. The still flask should not be more than 1/5 full and the mixture must be stirring freely using a magnetic stir bar. If it is not, carefully attempt to break up any solid deposits in the flask using a large spatula. If this does not work, seek assistance from your supervisor.
4. In a fume hood cleared of all other reactions and equipment, set up a reaction apparatus as illustrated in the attached scheme. Securely clamp the still flask and all other parts of the apparatus to a sturdy lab-stand or support rod.
5. Make sure that there is an ample supply of nitrogen or argon that will last at least 24 hours with a slow rate of bubbling and establish that both nitrogen/argon and cooling water are flowing at a reasonable rate with the hose connections to the condenser secured by copper wire or similar.
6. If the solvent still contains **sodium or potassium**:
 - a) With stirring, slowly add an equal volume of toluene or preferably xylene to the flask (see attached figure) while maintaining a slight counter-flow of nitrogen or argon through the apparatus. The counter-flow should be maintained during any additions to the flask throughout the entire procedure. Stir for 5-10 min. observing the reaction.

SOLVENT STILLS
PROCEDURES FOR SET-UP, USE, AND NEUTRALIZATION
 (continued)

- b) With stirring, add 1 ml of n-butanol or t-butanol and observe the reaction. In the presence of active metal hydrogen gas evolution will occur. Further 1 ml portions of the alcohol are added at such a rate that the heat evolved by neutralization does not cause the reaction mixture to come to reflux. This will take several hours, or even longer. The reactivity of the mixture can be monitored by briefly interrupting the nitrogen flow and monitoring the bubbler. As long as there is gas evolution from the apparatus, reactive metal is present.
- c) When no further reactivity is observed, procedure b) is repeated with ethanol. Again this may take several hours, or overnight, until all hydrogen evolution ceases.
- d) Add 50-100 ml methanol in 5 ml portions and monitor the reaction. Stir at least 1 h or until no further gas evolution is observed.
- e) Repeat procedure b) with water until no further gas evolution is observed.
- f) Dispose of the contents of the flask as organic chemical waste from your laboratory.
7. If the solvent still contains **lithium aluminum hydride**:
- a) With stirring, slowly add 1 ml portions of 95 % ethanol to the flask containing the hydride in solution (see attached figure) while maintaining a slight counter-flow of nitrogen or argon through the apparatus. The counter-flow should be maintained during any additions to the flask throughout the entire procedure. Stir for 5-10 min. observing the reaction.
- b) When no more gas evolution is observed slowly add a saturated solution of ammonium chloride.
- c) Separate the organic and aqueous layers formed.
- d) Dispose of the two components in the appropriate manner, i.e., the organic layer into the organic waste collection container, the aqueous layer into the aqueous waste collection container in your laboratory.
8. If the solvent still contains **calcium hydride in dichloromethane (CH₂Cl₂)**:
- a) With stirring, slowly add 1-2 ml portions of methanol to the flask (see figure) while maintaining a slight counter-flow of nitrogen or argon through the apparatus.
- The counter-flow should be maintained during any additions to the flask throughout the entire procedure. Stir for 5-10 min. after each addition observing the reaction.



SOLVENT STILLS
PROCEDURES FOR SET-UP, USE, AND NEUTRALIZATION
(continued)

- b) When no more gas evolution is observed slowly add excess water.
- c) Separate the organic and aqueous layers formed.
- d) Dispose of the two components in the appropriate manner, i.e., the organic layer into the halogenated organic waste collection container, the aqueous layer into the aqueous waste collection container in your laboratory.

COLUMN PURIFICATION SYSTEMS

Commercially available column purification systems are a viable alternative for some distillation procedures. While the column method does not have the fire or explosion initiators that distillation units have, they do, however, have their own set of safety considerations that must be accounted for.

1. The quantities of solvents in the system tend to be larger so the units must be used in an appropriate location equipped with flammable liquid cabinets, fire doors, sprinklers, and the quantity limits imposed by the building codes must not be exceeded.
2. The columns are pressurized from 5-50 psi therefore; they must be secure and equipped with the appropriate valves and plumbing.
3. Peroxides may accumulate on the columns and must be changed in accordance with the manufacturer's recommendation.
4. Some solvents, including tetrahydrofuran and methylene chloride, are incompatible with the copper catalyst therefore; the column method may not be suitable for some applications.

References: Cournoyer, Michael E., and Dare, Jeffery H., The Use of Alternative Solvent Purification Techniques, *Chemical Health and Safety*, July/August, 2003.

PERSONAL PROTECTIVE EQUIPMENT PROCEDURES FOR SELECTION AND USE

Personal protective equipment (PPE) is selected based on the potential hazard presented by the work. Each laboratory procedure should be scrutinized individually for potential hazards based on the chemicals to be used and the procedure to be performed. The hazard assessment is then used to determine the appropriate personal protective equipment.

Each laboratory group is responsible for assessing the potential hazards presented by their work. The Personal Protective Equipment Hazard Assessment Form found in Appendix B can be used for this purpose. The potential hazards presented by typical laboratory procedures and the corresponding personal protective equipment are found on the form. The list does not include all laboratory procedures. Additional tasks and personal protective equipment should be added as necessary on the form.

A list of chemicals that require skin protection can be found in Appendix C. These chemicals have been identified by the Occupational Safety and Health Administration (OSHA) and/or the American Conference of Governmental Industrial Hygienists (ACGIH) as chemicals that present a significant risk of skin absorption and subsequent toxicity. Many chemicals not on the list also require the use of gloves and other personal protective equipment. Never underestimate the risk of exposure. Always practice good chemical hygiene and use personal protective equipment.

HAND PROTECTION

No glove is resistant to all chemicals. Consult the glove manufacturer's selection guides for chemical compatibility prior to use. Glove selection guides are available in the chemistry or biology stockrooms and can also be found at the manufacturers web sites and through the EH&S web page (www.ehs.indiana.edu). For further assistance contact EH&S (855-6311).

When selecting and using gloves always:

- Consider chemical resistance, thickness, length, and dexterity requirements.
- Inspect all gloves before use for signs of swelling, cracking, discoloration, pinholes, etc.
- Double gloving (wearing one glove over another) can be used as a precaution.
- Change gloves frequently or as often as needed if they become contaminated.
- Do not touch doorknobs, phones, etc. when wearing gloves. (Remove them before touching anything to prevent leaving chemical residue on the item.)
- Remove gloves by pinching the material in the palm and turning them inside out as the glove is removed over the finger tips (thus keeping contamination on the inside of the removed glove.)
- Thicker reusable gloves should be rinsed after every use.

Chemical resistance is based on several characteristics of the glove material. When selecting the appropriate glove, the following properties should be considered:

- Degradation
- Breakthrough time
- Permeation rate

PERSONAL PROTECTIVE EQUIPMENT PROCEDURES FOR SELECTION AND USE

(continued)

Degradation is the change in one or more of the physical properties of a glove caused by contact with a chemical. Degradation typically appears as hardening, stiffening, swelling, shrinking or cracking of the glove. Degradation ratings indicate how well a glove will hold up when exposed to a chemical. When looking at a chemical compatibility chart, degradation is usually reported as E (excellent), G (good), F (fair), P (poor), NR (not recommended) or NT (not tested).

Breakthrough time is the elapsed time between the initial contact of the test chemical on the surface of the glove and the analytical detection of the chemical on the inside of the glove.

Permeation rate is the rate at which the test chemical passes through the glove material once breakthrough has occurred and equilibrium is reached. Permeation involves absorption of the chemical on the surface of the glove, diffusion through the glove, and desorption of the chemical on the inside of the glove. Resistance to permeation rate is usually reported as E (excellent), G (good), F (fair), P (poor), NR (not recommended), or NT (not tested). If chemical breakthrough does not occur, then permeation rate is not measured and is reported ND (none detected).

Manufacturers stress that permeation and degradation tests are done under laboratory test conditions, which can vary significantly from actual conditions in the work environment. Users may decide to conduct their own tests, particularly when working with highly toxic materials or chemicals for which no data can be found. This should always be done carefully in a fume hood with PPE and without touching the chemicals or contaminated materials with the hands (i.e. use forceps).

For mixtures, it is recommended that the glove material be selected based on the shortest breakthrough time.

The following table shows the typical glove materials and their general uses.

Glove Material	General Uses
Butyl	Offers the highest resistance to permeation by most gases and water vapor. Especially suitable for use with esters and ketones.
Neoprene	Provides moderate abrasion resistance but good tensile strength and heat resistance. Compatible with many acids, caustics and oils.
Nitrile	Excellent general duty glove. Provides protection from a wide variety of solvents, oils, petroleum products and some corrosives. Excellent resistance to cuts, snags, punctures and abrasions.
PVC	Provides excellent abrasion resistance and protection from most fats, acids, and petroleum hydrocarbons.
PVA	Highly impermeable to gases. Excellent protection from aromatic and chlorinated solvents. Cannot be used in water or water-based solutions.
Viton	Exceptional resistance to chlorinated and aromatic solvents. Good resistance to cuts and abrasions.
Silver Shield	Resists a wide variety of toxic and hazardous chemicals. Provides the highest level of overall chemical resistance.
Natural rubber	Provides flexibility and resistance to a wide variety of acids, caustics, salts, detergents and alcohols. (See Latex Gloves and Related Allergies below).

PERSONAL PROTECTIVE EQUIPMENT PROCEDURES FOR SELECTION AND USE

(continued)

Latex Gloves and Related Allergies

Allergic reactions to natural rubber latex can sometimes occur. The term "latex" refers to natural rubber latex and includes products made from dry natural rubber. Natural rubber latex is the product manufactured from a milky fluid derived mainly from the rubber tree, *Hevea brasiliensis*. Natural rubber latex is found in many products including gloves, personal protective equipment, medical equipment, office supplies, household products, automotive products, and childrens toys.

Several chemicals are added to this fluid during the processing and manufacture of commercial latex. Some proteins in latex can cause a range of mild to severe allergic reactions. The total protein serves as a useful indicator of the exposure of concern. The chemicals added during processing may also cause skin rashes. Several types of synthetic rubber are also referred to as "latex," but these do not release the proteins that cause allergic reactions.

Latex exposure symptoms include skin rash and inflammation, respiratory irritation, asthma and shock. The amount of exposure needed to sensitize an individual to natural rubber latex is not known, but when exposures are reduced, sensitization decreases.

In addition to skin contact with the latex allergens, inhalation is another potential route of exposure. The proteins responsible for latex allergies have been shown to fasten to powder that is used on some latex gloves. Latex proteins may be released into the air along with the powders used to lubricate the interior of the glove.

The following actions are recommended to reduce exposure to latex:

- Whenever possible, substitute another glove material.
- If latex gloves must be used, choose reduced-protein, powder-free latex gloves.
- Wash hands with mild soap and water after removing latex gloves.

Once a worker becomes allergic to latex, special precautions are needed to prevent exposures during work. Certain medications may reduce the allergy symptoms, but complete latex avoidance is the most effective approach.

PROTECTIVE EYEWEAR

Protective eyewear is *required* whenever there is a reasonable probability that the eyes could be exposed to chemicals. The type of eyewear required depends on the hazard classification of the area and procedure to be performed.

Types of Protective Eyewear

Safety Glasses

Safety glasses have shatter resistant lenses made of materials like polycarbonate plastic with side shields attached to the temples that meet the specifications of the American National Standards Institute Standard Z87.1-1989. Safety glasses are designed to stop physical objects or harmful radiation such a laser light from entering the eyes and provide little or no protection from vapors or liquids.

PERSONAL PROTECTIVE EQUIPMENT PROCEDURES FOR SELECTION AND USE

(continued)

Goggles

Properly vented safety goggles are the preferred eye protection to be worn when chemicals are handled in the laboratory. These should be worn *over* prescription glasses.

Goggles come in two types, vented and non-vented. Non-vented goggles are used to protect your eyes from vapors, mists, fumes, or other eye hazards that require complete eye coverage with no leaks or perforations.

Vented goggles are used where there are moderate quantities of liquids being used but no vapors or mists are involved. There are several types of vented goggles. The type of vented goggles made for laboratory use has a series of buttons embedded into the plastic. These buttons house a baffle plate that allows air to pass but presents a physical barrier to liquids. Do not use the common vented goggle with simple holes drilled in the sides. This type of vented goggle will not stop liquids from coming in through the holes and is not suitable for laboratory work.

Face Shields

Face shields are designed to augment other types of eye protection and are not meant to be a stand alone form of eye protection. Face shields are used to protect your entire face to catch any liquids that might splash onto the face.

Hazard Classifications

Areas and operations within research buildings can be classified into three types of hazardous areas based on the following definitions. It is important to recognize that the procedure is classified as well as the area. If a procedure creates a greater hazard than the laboratory classification would indicate, eye and face protection appropriate for the hazard shall be worn. It would be possible to have a Class 3 operation in a Class 2 area. Appropriate additional protection would be required.

Class 1 – Eye Protection Not Required

This classification includes laboratories that do not use chemicals, biological materials, or physically hazardous materials. Hazards requiring eye protection are seldom encountered in this area. These areas are exempt from the requirement that occupants and visitors must wear industrial safety glasses. Examples include computer or imaging laboratories and other areas such as:

- Offices including enclosed offices within laboratories or protected desk areas. To comply with this policy there must be a line of sight barrier (for example an office partition) between personnel and any chemicals or any chemical process in the laboratory.
- Conference rooms
- Libraries and reading rooms
- Corridors, lobbies, elevators, and stairwells
- Locker and rest rooms
- Mail and copier rooms
- Computer and computer user rooms
- Lounges and break rooms

PERSONAL PROTECTIVE EQUIPMENT PROCEDURES FOR SELECTION AND USE

(continued)

Class 2 – Eye Protection Required When Hazards Exist

This classification includes laboratories that use chemicals, biological materials, or physically hazardous materials on an occasional basis. Eye protection must be worn when the hazards exist. Safety eyewear such as industrial safety glasses with side shields are required for workers and visitors in these areas. Examples include laser laboratories and some research laboratories.

Class 3 – Eye Protection Required At All Times

Specific and predictable eye hazards exist in these areas such as laboratories that routinely use chemicals, biological materials, or machinery. Examples of eye protection required in these areas are acid splash goggles, face shields, welding helmets, and laser goggles. Industrial safety glasses alone may not provide adequate eye protection in these areas. Examples include chemistry teaching laboratories and organic chemistry laboratories.

Note: Contact lenses may complicate treatment in the event of an accident. They may be allowed or prohibited based on the specific laboratory procedures and policy. The use of contact lenses is only allowed in conjunction with appropriate safety eyewear and the laboratory supervisors approval. Instructors or supervisors must be aware of those wearing contact lenses.

Exemption Procedure

Eye protection may need to be removed while viewing materials through a microscope or similar equipment. Eye protection must be replaced after operation is complete. Microscope and similar equipment must be located in an area where removal of eye protection does not place personnel at risk from other hazards in the area.

Local Safety Procedure Required

State if eye protection can be removed behind a line of sight barrier. Define the line of sight barrier. Any approved exemptions must be identified on the Personal Protective Equipment Hazard Assessment Form LCS-4 in Appendix B.

PROTECTIVE CLOTHING

Protective clothing in the form of lab coats, aprons, and closed toed shoes are required whenever the possibility of chemical contamination to the body exists. Protective clothing that resists physical and chemical hazards should be worn over street clothes.

Lab coats and aprons should be left in the laboratory and not taken home. This prevents the worker from carrying incidental contamination out of the laboratory and presenting a chemical hazard to co-workers, friends, or family.

Disposable outer garments such as Tyvek suits, aprons, and lab coats may be useful when cleaning and decontamination of reusable clothing is difficult.

PERSONAL PROTECTIVE EQUIPMENT PROCEDURES FOR SELECTION AND USE

(continued)

Shorts, loose clothing (including ties), or torn clothing are inappropriate for work with hazardous chemicals.

Lab Coats

Lab coats are appropriate for minor chemical splashes and spills. They should be worn buttoned with the sleeves covering the arms. Do not roll up the sleeves.

Aprons

Rubber or plastic aprons are appropriate for handling corrosives or irritating liquids.

FOOTWEAR

Shoes should be worn at all times where chemicals are stored or used. Perforated shoes, sandals or cloth sneakers should not be worn in laboratories. They offer no barrier between the laboratory worker and chemicals or broken glass. Leather shoes are preferable but tend to absorb chemicals and may have to be discarded if contaminated with a hazardous material.

Chemical resistant overshoes, boots, or disposable shoe coverings (“booties”), may be used to avoid possible exposure to corrosive chemicals or large quantities of solvents or water that might penetrate normal footwear (e.g., during spill cleanup).

Although generally not required in most laboratories, steel-toed safety shoes may be necessary when there is a risk of heavy objects falling or rolling onto the feet, such as in bottle-washing operations, animal care facilities, or if large quantities of liquids are stored and moved in drums.

RESPIRATORY PROTECTION

Respiratory protection is typically provided by using adequate engineering controls such as chemical fume hoods, canopy hoods, snorkel hoods, glove boxes, and appropriately equipped biological safety cabinets. It should be noted that not all biological safety cabinets provide protection from toxic chemical vapors and fumes. These devices should be carefully selected and used only for their intended purpose.

A respirator may only be used when engineering controls, such as general ventilation or a fume hood, are not feasible or do not reduce the exposure of a chemical to acceptable levels. Respirators can only be used in accordance with the Occupational Safety and Health Administrations (OSHA) Respiratory Protection Standard and the Indiana University Respiratory Protection Program. Contact EH&S (855-6311) for more information or to obtain a respirator and arrange the required respirator fit test and medical examination.

HEAD PROTECTION

Head protection may be necessary in industrial type laboratories where overhead hazards exist or fluids may splash onto the head. Appropriate head protection in the form of hard hats or fluid barrier hats should be used in these cases. Hooded disposable coveralls may also be used if necessary.

PEROXIDE FORMING CHEMICALS AND OTHER TIME SENSITIVE MATERIALS PROCEDURES FOR SAFE HANDLING AND MANAGEMENT

Some laboratory chemicals known as time sensitive chemicals can become dangerous with age. This can be due to chemical reactions, over-pressurization of containers, toxicity, and other hazardous properties. For this reason handling and management of time sensitive chemicals are of particular importance. These chemicals include:

- Picric acid and other multi-nitro aromatics.
- Chloroform.
- Anhydrous hydrogen fluoride and hydrogen bromide.
- Liquid hydrogen cyanide.
- Formic acid.
- Alkali metals (K, Na, Li).
- Chemicals that form peroxides upon aging.

Other relevant sections of this plan include; Section 3.2, Procedures for Proper Labeling, Storage, and Management of Chemicals; Section 3.7, Reactive Chemicals; and the table of Peroxide Forming Chemicals in Appendix C.

PICRIC ACID AND OTHER MULTI-NITRO AROMATICS

Picric acid ($C_6H_3N_3O_7$ and other multi-nitro aromatics) can be extremely dangerous if allowed to dry. Picric acid with a moisture content of greater than 30% is considered a flammable solid by the Department of Transportation (DOT). Picric acid with a moisture content of less than 30% is considered a Class 1.1D explosive by DOT and is very shock sensitive. **DO NOT OPEN OR MOVE** a container of dry picric acid.

CHLOROFORM

Chloroform ($CHCl_3$) reacts with air to form phosgene gas (CCl_2O) which has a very low IDLH (Immediately Dangerous to Life or Health) value of 2 parts per million. Always open chloroform in a fume hood.

FORMIC ACID

Formic acid (90-100% CH_2O_2) decomposes to form carbon monoxide and water ($CO + H_2O$). Greater than 100 psi can develop with prolonged storage of 1 year or greater which is sufficient to break a sealed glass container. Vent containers frequently and read the product literature. Some have pressure relief caps and some Material Safety Data Sheets may recommend refrigeration.

**PEROXIDE FORMING CHEMICALS
AND OTHER TIME SENSITIVE MATERIALS
PROCEDURES FOR SAFE HANDLING AND MANAGEMENT**
(continued)

ANHYDROUS HYDROGEN FLUORIDE AND HYDROGEN BROMIDE

Anhydrous hydrogen fluoride (and hydrogen bromide) are a liquid phase above 15 psi. Stored in carbon steel cylinders (lecture bottles) they can react with the steel to form iron fluoride and hydrogen gas. Lecture bottles have a typical working pressure of 1800 psi and these chemicals have a 2 yr shelf life. Several anhydrous hydrogen fluoride cylinders have failed (> 2,400 psi) after 14-24 years of storage although there have been no reported problems with hydrogen bromide.

LIQUID HYDROGEN CYANIDE

Liquid hydrogen cyanide (CHN) is a liquid that boils at 26° C and is stored in low pressure cylinders. With no stabilizer (1% sulfuric acid) present polymerization can occur plus the production of ammonia which also helps catalyze the process. A crust can form on the liquid that, when jarred, can break off and fall into the liquid causing rapid exothermic polymerization and rupture of the cylinder causing fragmentation and release of this acutely toxic gas.

ALKALI METALS

The alkali metals (Li, Na, K, and NaK alloys) can react with dissolved oxygen when stored under mineral oil to form oxides and superoxides that can catch fire upon cutting. The oxidation forms a yellow or orange crust or coating. Lithium stored under nitrogen can form nitrides and the formation of the nitride is autocatalytic and can eventually autoignite.

PEROXIDE FORMING CHEMICALS

The peroxide forming chemicals include common organic solvents and can react with atmospheric oxygen to undergo autoxidation, or peroxidation, producing unstable and dangerous organic peroxides and hydroperoxides.

Formation of peroxides is accelerated by light and heat. Substances which have undergone peroxidation are sensitive to thermal or mechanical shock and may explode violently. All laboratory workers must learn to recognize and safely handle peroxidizable compounds. Peroxide forming substances include: aldehydes, ethers (especially cyclic ether), compounds containing benzylic hydrogen atoms, compounds containing the allylic structure (including most alkenes), vinyl and vinylidene compounds. A list of these chemicals can be found in Appendix C.

Safe Handling and Usage

- Labels on peroxide forming substances must contain the date the container was received, the date it was first opened, and the initials of the person who first opened the container.
- Include a notice such as **Warning-Peroxide Former** on the container.

**PEROXIDE FORMING CHEMICALS
AND OTHER TIME SENSITIVE MATERIALS
PROCEDURES FOR SAFE HANDLING AND MANAGEMENT**
(continued)

- Check for the presence of peroxides before using, and quarterly while in storage (peroxide test strips are available).
- If peroxides are found, the material should be decontaminated, if possible, or disposed through EH&S.
- The date and results of any testing should be placed on the container label.
- Never use a metal spatula with peroxides. Contamination by metals or disturbance of the crystals can lead to explosive decompositions.
- Store peroxides and peroxide forming compounds at the lowest possible temperature, away from light and heat.
- Refrigerators must be designed for the storage of flammable substances.
- Test for peroxides before distilling or evaporating peroxidizable solvents. After testing never distill substances contaminated with peroxides.
- If peroxides are present useable solvents may be treated to remove the peroxides.
- **Do not open or test the contents of the container** if 1) crystals are visibly present on or in the container or lid, 2) if a precipitate has formed or an oily viscous layer is present, or 3) if the container has been opened but not tested and is more than two years old. Call the Office of Environmental Health and Safety (EH&S) at 855-6311 for assistance.
- If the peroxide forming substance has been opened and more than one year has passed the material should be discarded.
- Dispose of Class III (see table in Appendix C) peroxidizable solvents within one year of purchase if unopened or 6 months of the opening.

Testing

The following test procedures may be used on most organic solvents. However, there is not a suitable, simple test procedure for detection of peroxides in substances such as alkali metals, alkali metal alkoxides, amides, or organometallics. **Do not test or treat any peroxide forming chemicals if you are unsure of the age, if there are visible crystals, or if a precipitate or oily viscous layer is present.**

Iodide Test:

Add 0.5-1.0 ml of the solvent to be tested to an equal volume of glacial acetic acid to which has been added about 0.1 g of sodium iodide or potassium iodide crystals. A yellow color indicates a low concentration of peroxide in the sample; a brown color indicates a high concentration. A blank determination should be made. Always prepare the iodide/acetic acid mixture at the time the test is made, because air oxidation slowly turns the blank to a brown color.

**PEROXIDE FORMING CHEMICALS
AND OTHER TIME SENSITIVE MATERIALS
PROCEDURES FOR SAFE HANDLING AND MANAGEMENT
(continued)**

Ferrous Thiocyanate Test:

A drop of the solvent to be tested is mixed with a drop of sodium ferrothiocyanate reagent which is prepared by dissolving 9 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in 50 ml of 18% hydrochloric acid. Add 0.5-1.0 g granulated zinc followed by 5 g sodium thiocyanate. When the transient red color fades, add 12 g more of sodium thiocyanate and decant the liquid from the unused zinc into a clean stoppered bottle. Pink or red coloration indicates the presence of peroxides.

Peroxide Test Strips:

The use of peroxide test strips is perhaps the most convenient method to test for the presence of peroxides. Test strips are commercially available from several vendors including:

- Gallade Chemical - Cat. No. 10081, www.galladechem.com, (888) 830- 9092
- Laboratory Safety Supply - Cat. No. 1162, www.labsafety.com, (800) 356-0783

Follow the manufacturer's instructions for using the strips to ensure adequate colorimetric detection. EH&S recommends disposal of any chemicals that test positive for peroxides because the positive test indicates they are aging and beginning to form peroxides. Concentrations at or above 100 PPM must be turned in to EH&S for disposal.

Treatment

Useable chemicals may be treated prior to use. Chemicals intended for EH&S disposal do not need to be treated. Any of the following procedures may be used to remove the peroxides. One of the above test procedures should be employed following treatment to ensure that peroxides have been removed. **Do not test or treat any peroxide forming chemicals if you are unsure of the age, if there are visible crystals, or if a precipitate or oily viscous layer is present.**

Method 1 - Activated Alumina:

Peroxides can be removed by passing the solvent through a short column of activated alumina. This method is effective for both water-insoluble and water-soluble solvents (except low molecular weight alcohols). Since this method does not destroy peroxides the alumina should be flushed with a dilute acid solution of potassium iodide or ferrous sulfate following treatment to remove peroxides from the alumina.

Method 2 - Ferrous Salt:

Peroxide impurities in water-soluble solvents are easily removed by gently shaking with a concentrated solution of a ferrous salt. A frequently used ferrous salt solution can be prepared either from 60 g of ferrous sulfate + 6 ml concentrated sulfuric acid + 110 ml water; or from 100 g of ferrous sulfate + 42 ml of concentrated hydrochloric acid + 85 ml of water.

NANOTECHNOLOGY SAFETY PROCEDURES

Nanomaterials are defined as ultrafine particles with a dimension of one to 100 nanometers in diameter. One nanometer is one-billionth of a meter.

Low-solubility ultrafine particles are more toxic than larger particles on a mass for mass basis. In addition to the hazardous properties of the chemical constituents, their smaller dimensions, larger surface area, and ability to penetrate cell membranes more easily than larger particles add to the hazardous properties of these materials.

Because of their small particle size, they can be deposited deep into the lungs and, once in the bloodstream, may be able to cross the blood-brain barrier. Exposure to these materials during synthesizing processes and use may occur through inhalation, ingestion, and contact with the skin or eyes.

Other hazards to consider are catalytic effects and fire or explosion. Particles in the nanometer size range are currently being evaluated for toxicity and critical exposure levels based on mass, surface area, and the number of particles per unit volume. Until these factors are determined workers should implement stringent controls on exposure when working with them.

The following guidelines, modified from the American Chemical Society, are provided to educate and protect those working with nanomaterials.

LAB SAFETY GUIDELINES FOR HANDLING NANOMATERIALS

1. Use good general laboratory safety practices as found in this *Laboratory Chemical Safety Plan*. Wear gloves, lab coats, safety glasses, face shields, closed-toed shoes as needed.
2. Be sure to consider the hazards of precursor materials in evaluating process hazards. OSHA's "Particularly Hazardous Substances" (such as cadmium) must be handled in a containment such as a fume hood or a glove box.
3. Avoid skin contact with nanoparticles or nanoparticle-containing solutions by using appropriate personal protective equipment. Do not handle nanoparticles with your bare skin.
4. If it is necessary to handle nanoparticle powders outside of a HEPA-filtered powered-exhaust laminar flow hood, wear appropriate respiratory protection. The appropriate respirator should be selected based on professional consultation with EH&S.
5. Use fume exhaust hoods to expel fumes from tube furnaces or chemical reaction vessels.
6. Dispose of and transport waste nanoparticles according to the hazardous chemical waste guidelines.
7. Vacuum cleaners used to clean up nanoparticles should be factory tested, HEPA-filtered units.
8. Equipment previously used to manufacture or handle nanoparticles should be evaluated for potential contamination prior to disposal or reuse for another purpose.
9. Lab equipment and exhaust systems should also be evaluated prior to removal, remodeling, or repair.
10. Given the differing synthetic methods and experimental goals, no blanket recommendation can be made regarding aerosol emissions controls. This should be evaluated on a case by case basis.
11. Consideration should be given to the high reactivity of some nanomaterials with regard to potential fire and explosion hazards.

SAFETY PROCEDURES FOR SETUP AND OPERATION OF HOT OIL BATHS AND OTHER HEATING SOURCES

Personal injury or property damage can result from the use of hot oil or sand baths and other heating sources in the laboratory. Personal hazards include injury and burns from hot surfaces, liquids, vapors or flames. Contact burns may occur and range from minor to severe.

Use of these devices are frequently left unattended and must be monitored. Sources of ignition exist from electrical components, hot surfaces, hot liquids, or open flames. Uncontrolled fire or explosion may result in severe personal injury or injury to others and/or widespread property damage.

The following procedure applies to, but is not limited to, all of the following devices:

- Ovens
- Hot plates
- Heating mantles and tapes
- Oil baths
- Salt baths
- Sand baths
- Hot-air guns
- Microwave ovens

ADMINISTRATIVE CONTROLS AND SETUP

Unattended Operations

- All unattended operations must have prior approval from the Principal Investigator.
- Provide for containment of materials in the event of spills or failures.
- Label all containers and process equipment with the name of the material and special hazards.
- Post emergency numbers on the lab door.
- Keep lab lights on.

Ovens, Furnaces, Heating Mantles, and Other Devices

- Burners, induction heaters, ovens, furnaces, and other heat-producing equipment must be located a safe distance from areas where temperature-sensitive and flammable materials and compressed gases are handled.
- Drying ovens should only be used for their intended purpose and not overloaded with combustible materials.
- Always use the grounded three-prong plug on all electrical devices and when using variable transformers.
- Older models of Variacs will keep whatever is plugged into them electrically live even though the Variac is switched off. Touching this device and ground at the same time could complete a circuit with your body and lead to electrocution. Always disconnect a Variac from the outlet before working with the device plugged into it.

**SAFETY PROCEDURES
FOR SETUP AND OPERATION OF
HOT OIL BATHS AND OTHER HEATING SOURCES
(continued)**

- Check all glassware before using to ensure it's free of cracks and other imperfections. Do not use if in doubt.
- Discard heating mantles if the ceramic is cracked or the fiberglass is brittle or damaged.
- Do not use any electrical equipment if the wire insulation is cracked, frayed or wires are exposed in any way.

Hot Oil and Sand Baths

- Do not leave an operating sand or oil bath unattended unless it is equipped with a high-temperature shutoff and with a warning label.
- Know the flash point of the material when using oil baths. Consult the chemical manufacturer's technical information prior to use. NEVER heat a bath fluid above its flash point. Watch for smoking of the oil; oil that is smoking is too hot and may burst into flames at any moment. If an oil bath starts to produce smoke, turn off the heat immediately.
- Baths should be mounted on a laboratory jack that can be lowered easily without danger of the bath tipping over to cool the bath in an emergency. Equipment should be clamped high enough above a hot plate or oil bath that if the reaction begins to overheat, the heater can be lowered immediately and replaced with a cooling bath without having to readjust the clamps holding the equipment setup.
- Place equipment in a central location in the fume hood such that an uncontrolled fire does not melt the rubber seal surrounding the inspection ports located at the sides of the fume hood.
- When using hot oil or sand for heating, mount the baths in such a way that they cannot be overturned or that water cannot fall into an oil or sand bath causing hazardous splattering.
- Oil expands in volume when heated. Overfilling should be avoided.
- Secondary containment for oil baths must be used to contain any possible spills.
- All oil baths must be labeled with the name of the oil and its maximum safe working temperature:

“Hot Mineral (Silicone) Oil”

“Do not allow the temperature to exceed ____ deg C”

- Store the oil or sand for reuse in a covered secondary container that is labeled with the name and maximum safe working temperature.

ENGINEERING CONTROLS

- All unattended electrical heating equipment must be equipped with a manual reset over-temperature shutoff switch, in addition to normal temperature controls.
- Use non-mercury thermometers, thermocouples, or bimetallic temperature indicators. Do not use a sand or oil bath unless it is equipped with a thermometer (non-mercury) or other temperature indicating device.
- Use a temperature-control device and a high-temperature shut-off device.

**SAFETY PROCEDURES
FOR SETUP AND OPERATION OF
HOT OIL BATHS AND OTHER HEATING SOURCES
(continued)**

- Heating equipment with circulation fans shall be equipped with an interlock arranged to disconnect current to the heating elements if the fan fails.
- Heated Constant Temperature Baths: NEVER heat a bath fluid above its flash point.
- Electrically heated constant temperature baths shall be equipped with over-temperature shutoff switches in addition to normal temperature controls.

PERSONAL PROTECTIVE EQUIPMENT

- Appropriate gloves, safety glasses and lab coats must be worn when handling chemicals, containers, apparatus, and heating equipment.

EMERGENCY RESPONSE

- Regardless of the method used to heat something, a stuck contact, an electrical short circuit, uncontrolled chemical reaction, or other malfunction can cause a reaction to heat to dangerously high temperatures. Do not leave experiments unattended without prior approval, implementing proper precautions, and using the proper fail-safe devices.
- Know where the emergency gas shut off is for your lab when using Bunsen burners.
- Know where the nearest Fire Alarm Pull Box is to your lab.
- Know how to use a fire extinguisher. Activate the fire alarm FIRST and use only 1 fire extinguisher before evacuating the area.