NC State University

Environmental Health and Safety Center

Chemical Hygiene Plan (CHP)

1910.1450 OSHA Lab Safety Standard

Revision 1
May 2009

1. Purpose

The purpose of the Chemical Hygiene Plan is to acquaint students and employees with North Carolina State University's safety and health procedures and to inform employees of their rights and obligations under federal regulations regarding laboratory use of hazardous chemicals.

While the scope of this section is limited to hazardous chemicals, additional information regarding NC State health and safety requirements for other hazards, including but not limited to ionizing and non-ionizing radiation, biohazards, and the safe use of other hazardous materials and equipment can be found in the NC State Health and Safety Manual at: http://www.ncsu.edu/ehs/healthsafety_man.htm

The provisions of the NC State Chemical Hygiene Plan that follow will serve to minimize the risks associated with exposure to hazardous chemicals. In addition, care must be taken to assure that chemical use areas are secure. Each chemical user should review the NC State Lab Security and Safety Procedures at:
http://www.ncsu.edu/ehs/www99/right/handsMan/worker/lab_security.htm

2. Scope

a. What is the CHP?

The Chemical Hygiene Plan (CHP) applies to all North Carolina State University laboratory personnel, who handle and may be exposed to hazardous chemicals in research laboratories at North Carolina State University. The Chemical Hygiene Plan is in place to protect employees from specific health hazards in laboratories and to keep exposure below limits specified by OSHA. The Chemical Hygiene Plan shall be readily available to employees in laboratories at all times. The CHP shall include all elements required by OSHA 29 CFR 1910.1450.

b. What is not covered

The CHP does not cover work with radioactive materials or biological agents. Procedures for work with these materials area addressed via the University's Radiation Safety Manual and Biosafety Manual, respectively.
Furthermore, additional information on physical hazards such as electrical safety and fall protection that are not covered under CHP can be found on EHS website in the Health and Safety Manual:
http://www.ncsu.edu/ehs/healthsafety_man.htm

c. **Chemical hygiene officer**

The primary investigator (PI) should designate a person as chemical hygiene officer to coordinate and implement the CHP in their area. The University Chemical Hygiene Officer resides in the Environmental Health and Safety Center.

3. How to review this document

a. Basic CHP

The basic CHP includes all information that employees are required to review as part of their work or research assignment. Additional information is also provided as part of the optional modules section.

b. **Optional modules**

If the PI/Supervisor determines a laboratory employee needs additional health and safety information for using hazardous materials, the employee shall review the optional (additional) CHP modules/links. These modules will direct users to additional information on the NCSU website or other web-base resources.

4. The basic safety training and information you need

The Principal Investigator (PI) shall determine the extent of training. The PI shall also provide employees with information and training to ensure that they are apprised of the hazards of chemicals present in their work area.

a. **Managers Checklist**

Includes Specific Training for your work area. This checklist shall be provided at the time of an employee's initial assignment to a work and completed on the first day.

http://www.ncsu.edu/ehs/safetyplan/newemplo.pdf

b. Content of this CHP document

Including basic and optional modules shall be used as a training tool for current and new employees.

c. New Employee Orientation Training

This training is considered basic training, required for all new employees.

d. Specialized training that you need

Such information and training shall be provided at the time of an employee's initial assignment to a work area and prior to assignments involving new exposure situations the frequency of refresher information and training shall be determined by the PI. OSHA Laboratory Safety Standard requires that employee information and training shall cover the following elements:

- Contents of the OSHA Laboratory Safety Standard (29 CFR 1910.1450)
- The location and availability of the Chemical Hygiene Plan
- The permissible exposure limits for OSHA regulated substances (29 CFR part 1910, subpart Z) or recommended exposure limits for other hazardous chemicals where there is no applicable OSHA standard
- Signs and symptoms (see Materials Safety Data Sheet)
- Location and availability of known reference material on the hazards, safe handling, storage and disposal of hazardous chemicals found in the laboratory including, but not limited to, EH&S Health and Safety Manual, Material Safety Data Sheets received from the chemical supplier, and Materials and Waste Directory.
- Methods that may be used to detect presence of hazardous material in work environment. EH&S Gas monitoring Program requires gas approved-type of gas monitoring devices for any highly toxic, toxic, flammable, and/or pyrophoric gases. Plans to purchase monitoring equipment must be reviewed and approved by the Industrial Hygiene Section of the NCSU Environmental Health and Safety Center. If hazard assessment based on the factors such as toxicity, physical status, volume, frequency of use, and existence/using chemical hoods indicate any possible exposure above OSHA exposure limits or action levels, EH&S will perform personal and area monitoring. Please contact Environmental Health and Safety for any necessary monitoring /sampling for hazardous material.

- Employees need to be informed about the specific health and physical hazards of the chemicals in their work environment. MSDS and OSHA Occupational Health and Safety Standards are two major sources of this information.
- The measures employees can take to protect themselves from these hazards, including specific procedures the PI/Supervisor has implemented to protect employees from exposure to hazardous chemicals, such as appropriate work practices, emergency procedures, and personal protective equipment to be used.
- Safety training for specific hazards/procedures such as safe handling of pyrophoric chemicals or perchloric acid use.

e. Safety plan and self-assessment checklist

The PI shall train all employees on details of safety plan, how to obtain and to use it, and also use the Self Assessment Checklist as a support training tool.

f. Lab specific Standard Operating Procedures (SOP's)

As part of the Safety Plan, laboratories need to develop standard operating procedures that spell out each experiment, along with all safety precautions, necessary protective methods and equipment. SOPs need to be updated frequently and readily available for employees to use.

g. **Other training documents**

Document such as equipment operation manual, published literatures /procedures, etc.

5. Medical consultation and examination

Employees working with animals are required to complete a health questionnaire, which is reviewed by an occupational physician working for or with University. The questionnaire review will allow for appropriate medical recommendations to be provided to the employee and their supervisor for the work they will be performing.

Certain other employee tasks may require medical examinations. In the event of an overexposure to a toxic substance, the emergency phone number for the university should be called (911). As part of the responding action employees may be offered the opportunity for a medical exam or consultation related to their exposure.

http://www.ncsu.edu/ehs/www99/right/handsMan/worker/med.html

6. Hazard Determination/Identification and Assessment

a. Adequate Facility for Chemical Use

Before starting new research or modifying an existing research protocol, the PI needs to ensure that there are adequate facilities in place based on the type/classes of hazardous materials to be used. This includes, but is not limited to; eyewashes and safety showers, laboratory chemical hoods, gas cabinets, glove boxes, storage cabinets, gas detectors, fire detection/ extinguishing systems, etc.

i. Eyewash Stations

Eyewash stations are required for all laboratories utilizing chemicals hazardous to human eyes. An eyewash is considered as a **first aid** measure rather than a preventative measure. Proper exposure control methods, including eye protection is always required to minimize eye exposure to hazardous chemicals. To provide adequate protection, emergency eyewash stations need proper care and maintenance. PIs/supervisors need to train all students/employees on the location and proper use of eyewash stations. Eyewash installations must meet the ANSI Z358.1 guidelines for plumbed and self-contained eyewash stations. Testing requirements and other information is included at:

http://www.ncsu.edu/ehs/www99/right/handsMan/factsheet/Eyewash%20fact_1.pdf

ii. Safety Showers

Safety showers are required whenever the body may be exposed to injurious corrosive chemicals or any chemical hazardous to human skin. Safety showers are also considered to be a first aid measure rather than a preventative measure. Proper exposure control methods, including face, hand, and body protection are utilized to minimize skin exposure to hazardous chemicals. To provide adequate protection, safety showers need proper care and maintenance. PIs/supervisors need to train all students/employees on the location and proper use of safety showers. Emergency safety shower installations must meet the ANSI Z358.1 guidelines for plumbed and self-contained safety showers. Testing requirements and other information is included at:

http://www.ncsu.edu/ehs/www99/right/handsMan/factsheet/Safety_Shower_fact_1.pdf

iii. Adequate engineering controls

The PI shall ensure that the type/number of the engineering control devices and exhaust systems are appropriate for new/modified research. Refer to section 9, Hazard Control (engineering controls).

iv. Change and modifications

Any change in laboratory systems, such as adding local exhaust systems, requires a Facility Modification Request. This form ensures that modifications are made in such a way that system capacity, safety aspects and building code requirements are addressed.

b. Classes of Chemical Hazards: (Health and Physical hazards)

For proper storage and exposure prevention purposes, PIs need to be aware of different classes of chemical hazards. Materials listed as toxic, highly toxic, or which are indicated to be suspect or known carcinogens or reproductive hazards shall be used in exhausted enclosures such as laboratory chemical hoods. Substances which are not toxic, but which are corrosive and/or flammable, should also be used in exhausted laboratory chemical hoods since these hoods are equipped with a spill retention lip to contain spilled materials inside the hood. Small quantities of low toxicity flammable liquids, such as half pint squeeze bottles of ethyl alcohol or dilute solutions of acids or bases may be appropriate for bench top use. Materials where the effects are not known should be handled in a manner similar to those known to be highly toxic or carcinogenic.

Optional Modules:
OSHA 29 CFR 1910.1200 App A: Health Hazard Definitions

i. Toxic and Highly Toxic Agents

OSHA regulations (29 CFR 1910.1200 Appendix A) define toxic and highly toxic agents as substances with median lethal dose (LD_{50}) values in the following ranges:

Test	Toxic	Highly Toxic
Oral LD_{50} (Albino rats)	50-500 mg/kg	≤50 mg/kg
Skin Contact LD_{50} (Albino rabbits)	200-1000 mg/kg	≤200 mg/kg
Inhalation LC_{50} (Albino rats)	200-2000 ppm/air	≤200 ppm/air

It is important to note that the above classification does not take into consideration *chronic toxicity* (e.g. carcinogenicity and reproductive toxicity). Also, note that LD_{50} values vary significantly between different species, and the human toxicity for a substance may be greater or less than that measured in test animals. OSHA considers substances that are either toxic or highly toxic, as defined above, to be *particularly hazardous substances* (See section 13).

Optional Modules:
Appendix IV: **Chemical Toxicology**

ii. Corrosives

OSHA defines corrosive material as:
"A chemical that causes visible destruction of, or irreversible alterations in, living tissue by chemical action at the site of contact. For example, a chemical is considered to be corrosive if, when tested on the intact skin of albino rabbits by the method described by the U.S. Department of Transportation in appendix A to 49 CFR part 173, it destroys or changes irreversibly the structure of the tissue at the site of contact following an exposure period of four hours. This term shall not refer to action on inanimate surfaces".
See MSDS documents to find if a chemical is considered " corrosive"

Optional Modules:

1. **Appendix I, Corrosives**
2. **Corrosive material and their hazards**
3. **Working safely with corrosive liquids and solids**

iii. Carcinogens
See section 13.a for information

iv. Reproductive Toxins
See section 13.d for information

v. Sensitizer (Allergen)
A chemical that causes a substantial proportion of exposed people or animals to develop an allergic reaction in normal tissue after repeated exposure to the chemical.

vi. Flammables

a. Flammable material

A flammable material is any liquid, solid or gas that will ignite easily and burn rapidly. Materials that are flammable are of concern due to their ability to render damage to property and more importantly, to injure or cause death of workers. Flammable liquid refers to any liquid having a flash point below 100 ^{o}F. Flammable liquids need to be stored in a NFPA approved flammable storage cabinet.
For more information on flammable and combustible liquids, different classes, and proper storage, please see the following link:

http://www.ncsu.edu/ehs/www99/right/handsMan/lab/flam.html

b. Combustible Dust

Any combustible material (and some materials normally considered noncombustible) can burn rapidly when in a finely divided form. If such a dust is suspended in air in the right concentration, it can become explosive. The force from such an explosion can cause employee deaths, injuries, and destruction of entire buildings. Materials that may form combustible dust include *metals* (such as aluminum and magnesium*), wood, coal, plastics, biosolids, sugar, paper, soap, dried blood, and certain textiles*.

Optional Modules:

1. **OSHA** 29 CFR 1910.106: Flammable and combustible liquids
2. Combustible Dust in Industry: Preventing and Mitigating the Effects of Fire and Explosions

vii. Reactive chemicals and Reactive Interactions

a. ***Reactive Chemicals***

Reactive chemicals are materials that can be hazardous by themselves when caused to react by heat, pressure, shock, friction, a catalyst, or by contact with air or water. Air, light, heat, mechanical shock, water, and certain catalysts can cause decomposition of some highly reactive chemicals, liberating heat, toxic gases, or leading to an explosion. One must use specialized procedures and control equipment whenever working with reactive materials. The following table shows different classes of reactive chemicals:

Reactivity Hazard General Definition Examples	Reactivity Hazard General Definition Examples	Reactivity Hazard General Definition Examples
UNSTABLE (DECOMPOSING, THERMALLY SENSITIVE, SHOCK SENSITIVE, EXPLOSIVE)	Has the tendency to break down (decompose) over time or when exposed to conditions such as heat, sunlight, shock, friction, or a catalyst with the resulting decomposition products often being toxic or flammable. Decomposition can be rapid enough to give an explosive energy release and can generate enough heat and gases for fires/explosions.	Trinitrotoluene (TNT), dibenzoyl peroxide, ethylene oxide, acetylene, picric acid, hydrogen peroxide (concentrated)
POLYMERIZING	Has the tendency to self-react to form larger molecules, while possibly generating enough heat/gases to burst a container	Acrylic acid, styrene, 1,3-butadiene
PYROPHORIC	Will ignite spontaneously when exposed to air	Phosphorus, silane, lithium hydride
PEROXIDE FORMER	Has the tendency to slowly react with oxygen, such as from being exposed to air, to form unstable organic peroxides	1,3-Butadiene, isopropyl ether, ethyl ether
WATER REACTIVE	Will react with water or moisture. Some react slowly; others violently. Heat and flammable/toxic gases may be produced.	Sodium, sulfuric acid, acetic anhydride
OXIDIZER	Will give up oxygen easily or readily oxidize other materials.	Chlorine, nitric acid, perchloric acid

b. Chemical Reactions (Reactive interactions)

Reactive interactions require the combining of two or more materials to pose a hazardous situation by chemical reaction. Many materials that are not considered “reactive materials” can nevertheless react dangerously with other, incompatible materials. Incompatible materials must be sufficiently segregated in storage to prevent mixing during fires, explosions, and natural disasters like earthquakes. Accidents with incompatible materials often occur during the commingling of wastes in laboratories. At times, a material may be stored, or located intentionally in a certain area (addition of the right material, but in the wrong amount) or left by accident (such as contaminants like rust or lubricants).

Consult MSDS for list of incompatible chemicals.

See the following link for incompatible chemical groups:
http://www.ncsu.edu/ehs/www99/right/handsMan/lab/Storage%20Groups.pdf

Optional Modules:

1. **Appendix II, Reactive Chemicals**
2. **Appendix V, Explosives**
3. **OSHA:** Chemical Reactivity Hazard
4. Reactive Material Hazards
5. Essential Practices for Managing Chemical Reactivity Hazards
6. OSHA/CCPS Chemical Reactivity Hazard
7. OSHA: Explosive and Blasting Agents

c. Exposure prevention and assessment

i. Permissible Exposure Limits

For laboratory use (29 CFR 1910.1450) of OSHA regulated substances, the procedures set forth in this document are intended to control laboratory employees' exposures to levels which do not exceed the permissible exposure limits specified in 29 CFR part 1910, subpart Z.

ii. Exposure Assessment

a. Initial Monitoring: NC State EH&S (Industrial Hygiene group) conducts exposure assessment surveys of work areas to review safe work practices, to assess the potential for chemical exposure, and to recommend corrective action. OSHA requirements include air sampling, medical surveillance, and special handling procedures for certain materials and circumstances. Any new use of any of the substances in the following list should be immediately added to your chemical inventory, a copy of your updated inventory submitted to EH&S (Attn. Bruce Macdonald, Box 8007). Environmental Health and Safety (Roger_Lewis@ncsu.edu) must be notified when materials listed in Appendix C are obtained. After the initial notification has been made, frequent orders of the same material do not require notification.

If you have not yet provided this notification for a listed material, please consider this as new use for reporting purposes and supply the requested information. This will permit the necessary interaction to determine if air sampling, medical surveillance, or other appropriate handling procedures are necessary consistent with federal requirements.

b. Periodic monitoring: If the initial monitoring prescribed by paragraph (1) of this section discloses employee exposure over the action level (or in the absence of an action level, the PEL), the PI/Supervisor shall immediately comply with the exposure monitoring provisions of the relevant standard. Monitoring may be terminated in accordance with the relevant standard.

c. Employee notification of monitoring results: The PI/Supervisor shall, within 15 working days after the receipt of any monitoring results, notify the employee of these results in writing either individually or by posting results in an appropriate location that is accessible to employees. The University provides medical consultation for employees who may have been exposed to chemicals in excess of OSHA exposure limits.

7. MSDS and Labels

PIs/supervisors shall ensure that labels on incoming containers of hazardous chemicals are not removed or defaced. PIs shall maintain ready access to any material safety data sheets that are received with incoming shipments of hazardous chemicals, and ensure that they are readily accessible to laboratory employees. Where chemical purchase is done via electronic access to the vendors catalog, the MSDS should also be requested as part of the transaction and the copy received should be retained in the laboratory. The NC State University online MSDS database is located at:

http://www.ncsu.edu/ehs/MSDS.htm

8. Hazard Reviews

a. Operations/Procedures/Activities that require prior approval

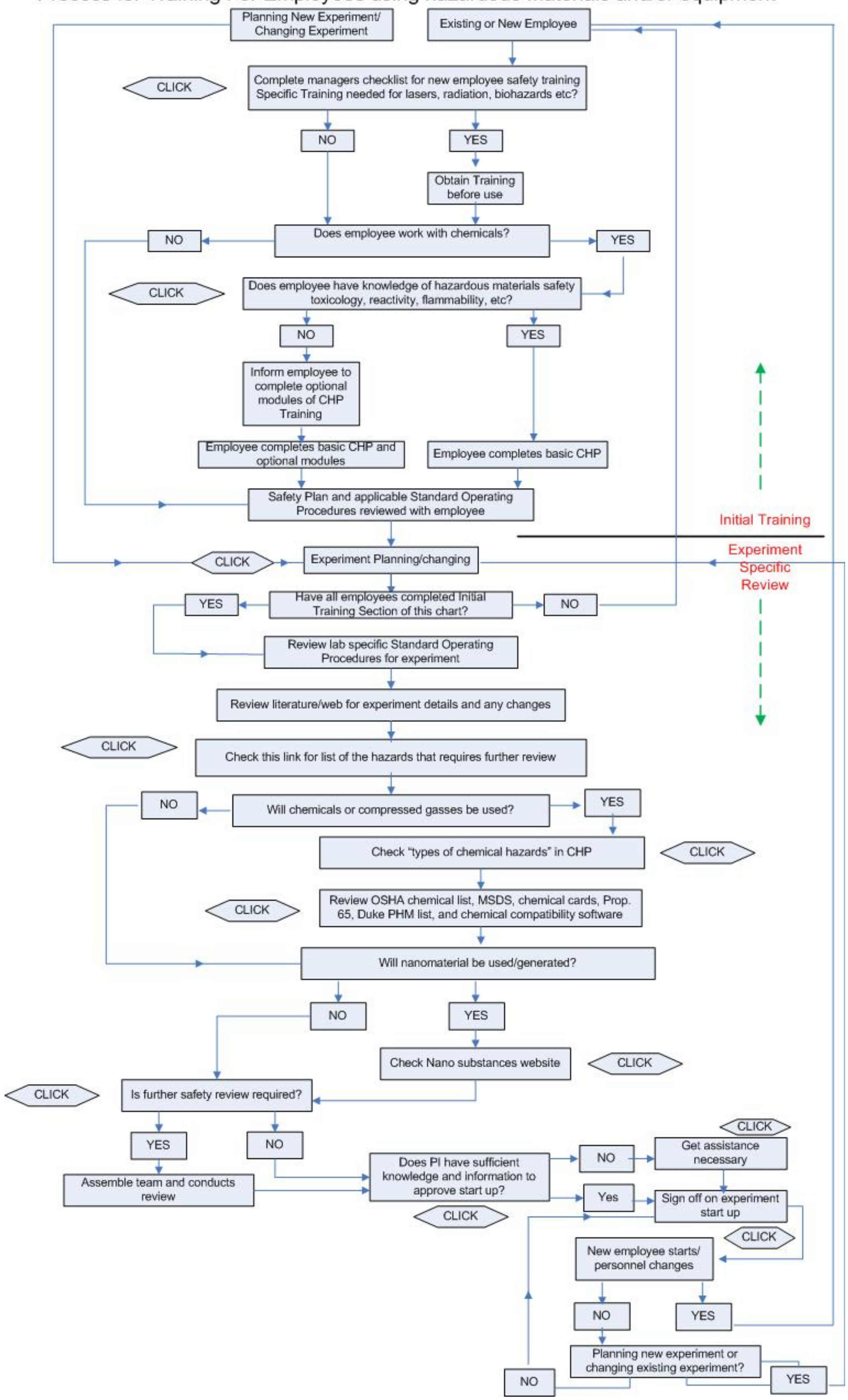
Routine lab operations should be conducted according to the practices listed in the American Chemical Society Publication "Safety in Academic Chemistry Laboratories". Operations involving new use of hazardous materials and/or equipment require a hazard review and needs to be approved by the PI.

In order to assure that appropriate safety equipment is obtained and to assure that appropriate safety controls are in place prior to the use of certain hazardous materials or equipment, please check Safety Reviews / Approvals at time of purchase. This is a listing of those items that need to be reviewed with Environmental Health and Safety personnel at the time of purchase. Further more, plans to purchase monitoring equipment must be reviewed and approved by the Industrial Hygiene Section of the NCSU Environmental Health and Safety Center.

As a matter of good practice, and to satisfy regulatory requirements, **particularly hazardous substances** require additional planning and considerations. Because of the high risk associated with these substances, laboratory employees planning to use a particularly hazardous substance must first receive explicit written approval from their Principal Investigator. A specific SOP shall be developed for these substances to include:

- Identity, physical characteristics, and health hazards of the substance involved
- Consideration for exposure control methods
- Plans for storage and secondary containment
- Plans for safe removal of contaminated waste
- Decontamination and spill procedures
- Emergencies
- Designated area

Process for Training For Employees using hazardous Materials and/or equipment



9. Hazard Control

Hazard Controls are an important component of the Chemical Hygiene Plan and shall include details of control measures to reduce employee exposure to hazardous chemicals including engineering controls, the use of personal protective equipment and administrative controls/work practices.

Particular attention shall be given to the selection of control measures for chemicals that are known to be extremely hazardous. (OSHA reg. chem. and 13 carcinogens) and as well as systemic toxins and reproductive hazards.

a. Substitution

Substituting in less hazardous chemicals (e.g., using proprietary detergents instead of chromic acid for cleaning glassware; or, using toluene instead of benzene for liquid-liquid extraction or chromatography) shall be considered when appropriate.

b. Engineering controls

Exposure to hazardous materials must be controlled to the greatest extent feasible by use of engineering controls. Contact EH&S for assistance in determining engineering controls necessary for your work situation. Engineering control methods include, but are not limited to, isolation, and using exhaust ventilation systems (laboratory chemical hoods, gas cabinets, glove boxes, biosafety cabinets, etc.).

i. **Local Exhaust Ventilation and Enclosures**

The primary purpose of local exhaust ventilation is to protect the employee from hazardous airborne exposures. Local exhaust ventilation systems include exhaust fans, their associated ductwork, and typically a work enclosure or material enclosure. In some cases, such as when materials are reactive with air or moisture, glove boxes may be required. Refer to the Material Safety Data Sheet to determine properties of materials for determination of appropriate engineering controls, storage, handling, work practices, and protective equipment.

Materials listed as toxic, highly toxic, or which are indicated to be suspect or known carcinogens or reproductive hazards shall be used in exhausted enclosures such as laboratory chemical hoods.

a. Use of chemical hoods and other protective equipment

Chemical laboratory hoods (fume hoods)

To protect laboratory employees from hazardous chemicals, chemical laboratory hoods must be used and functioning properly. Before using chemical laboratory hoods, lab employees need to ensure that the hood has been certified by EH&S, and posted by a green sticker. Any modifications to exhaust ventilation systems require completion and submission of Facilities Operations Modification Request Form.

b. Gas Cabinets

With the exception of cylinders containing a non-toxic, flammable gas in small quantity, and cylinders used in laboratory chemical hood applications, hazardous gas cylinders must be housed in gas cylinder cabinets.

c. Glove Box

Pyrophoric and water reactive chemicals are required to be stored and used under inert atmospheric conditions (i.e. a glove box). Any Glove Box shall meet the ANSI Z 9.5-2003 (or most recent version) requirements.

d. Other exhaust devices

Other exhaust devices such as snorkels and canopy hoods have limited applications and are not generally appropriate for hazardous chemical exposure control in laboratories. PIs shall train all employees and students to ensure that they are aware of use and limitations of different exhaust systems in laboratories. PIs shall also ensure that lab users are aware (training, SOPs, and postings) that biological safety cabinets and clean benches are not for chemical use and that they cannot provide protection against hazardous chemicals. Only biological safety cabinets that are 100% exhausted (class 2 B2 and above) can be used for chemical exposure control. Ductless hoods have multiple limitations for protection against chemical exposure and are not currently allowed for use at NC State University.

c. **Administrative control**

Administrative controls are procedural measures, which should be taken to reduce or eliminate hazards associated with the use of hazardous materials. Administrative controls include, but are not limited to the following:

- Careful planning of experiments and procedures with safety in mind. Planning includes the development of written work procedures for safe performance of the work.
- Restricting access to areas in which hazardous materials are used.
- Using signs or placards to identify hazardous areas (designated areas).
- Use secondary containers during storage of liquids.
- Store chemical by hazard class in appropriate cabinets. Do not store liquids above eye level.
- Micro-scaling the size of the experiment to reduce the amount of chemical usage.

d. Personal Protective Equipment (PPE)

Personal Protective Equipment:

Protective equipment, including personal protective equipment for eyes, face, head, and extremities, protective clothing, respiratory devices, and protective shields and barriers, shall be provided, used, and maintained in a sanitary and reliable condition wherever it is necessary by reason of hazards of processes or environment, chemical hazards, radiological hazards, or mechanical irritants encountered in a manner capable of causing injury or impairment in the function of any part of the body through absorption, inhalation or physical contact.

NC State University minimum PPE requirements include the use of a button style lab coat, eye protection and protective gloves. Additional PPE that may be required based on the hazard review. When pyrophoric or highly flammable chemicals are being used, fire rated lab coats (i.e. Nomex or similar products) would be required.

Respirators shall not be procured or used without prior approval from EH&S. This is necessary to assure proper medical authorization, proper selection, appropriate training, and other measures required by OSHA regulations to assure employee safety.
Link to respiratory protection program:
http://www.ncsu.edu/ehs/www99/right/handsMan/worker/resp/resp.html

Click the following for NC State University PPE guidelines:
http://www.ncsu.edu/ehs/www99/right/handsMan/worker/ppe/select.html

Optional Modules:
OSHA General requirements. –29 CFR 1910.132

10. **Chemical Storage and transfer**

Chemical Storage and Dispensing

Chemicals need to be stored based on their compatibility. Consult MSDS for proper storage method.
http://www.ncsu.edu/ehs/www99/right/handsMan/lab/Storage%20Groups.pdf

a. Quantities, Dispensing and Transfer (compatibility, cabinets, location)

Storage quantity needs to be maintained as minimum as possible. Flammables and combustible liquids need to be stored in a NFPA- approved flammable storage cabinet.
http://www.ncsu.edu/ehs/www99/right/handsMan/lab/flam.html

Avoid purchasing large chemical containers (e.g. 5-gallon or larger). This is due to increased risk of fire, spill, and exposure during transferring chemicals form a large container to smaller containers.
http://www.ncsu.edu/ehs/www99/right/handsMan/FlammableandToxicChemicalsDispensingSafety.pdf

b. Storage

- Storage areas must be clearly marked with the appropriate hazard warning signs.
- All containers (even if the material is in very small quantities such as 0.1%) must be clearly labeled with the chemical name or mixture components and the appropriate hazard warning information.
- Chemical storage areas must be secure to avoid spills or broken containers (e.g., cabinets closed)
- Storage areas or laboratory rooms must be locked when laboratory personnel are absent.

http://www.ncsu.edu/ehs/www99/right/handsMan/lab/Storage%20Groups.pdf

11. Safe Work Practices

a. Safe handling

- Designated areas (e.g., chemical hoods, glove boxes, lab benches, outside rooms, etc.) for material use must be established and the areas identified by signs or postings.
- Containment devices such as chemical hoods and personal protective equipment (gloves, lab coat, and eye protection) must be used when handling these hazardous substances.
- Procedures for the safe use of the material and waste removal must be established prior to use.
- Decontamination procedures must be developed in advance and strictly followed.
- Only laboratory personnel trained to work with these substances shall perform the work, and always within the designated area. Prior approval by principal investigator or supervisor is required.

Only the minimum quantity of the particularly hazardous substance necessary to conduct the research should be ordered and to the extent possible, the experimental design should be done on a micro-scale.

b. Standard Operating Procedures (SOPs)

All laboratories shall follow standard operating procedures, which include safety and health considerations, such as engineering and administrative controls and personal protective equipment (PPE). These SOPs should be procedures that are needed for your laboratory, which may not be adequately covered in your University Safety Plan.

http://www.ncsu.edu/ehs/safetyplan/index.html

Two references for additional standard operating procedures, both adopted for use by NC State University include:

- Safety in Academic Chemistry Laboratories
- NC State Health and Safety manual

Each of these reference materials should be used in conjunction with this document to augment the information in your Laboratory Safety Plan.

The sections from the Health and Safety Manual listed below are those, which include information pertinent to prevention of exposure to laboratory chemicals:

- Exhaust Ventilation for Hazardous Materials
- Hazard Reviews
- Hazard Communication
- Gas Monitoring Program
- Flammable and Combustible Liquids
- Exposure Prevention and Assessment
- Cryogenic Safety
- Compressed Gas Safety
- Chemical Hood Resources
- Lab Startup and Relocation
- Inspection Checklists
- Inspecting Laboratory Facilities

- Laboratory Safety
- Laboratory Security Guidelines
- Personal Protective Equipment
- Respiratory Protection Program
- Medical Surveillance
- Nano structures
- Reproductive health protection

12. **Provision of materials to others**

PIs are responsible to maintain an updated chemical inventory list. If a chemical is transferred to another PI, both receiving and transferring PIs shall update their chemical inventory lists.

Please remember that transferring chemicals such as **controlled substances** to other users is restricted and needs to comply with federal and state regulations.

13. **Particularly Hazardous Substances (classes and specific protective measures)**

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

While review of the Material Safety Data Sheet is necessary to understand hazard properties such as flammability, reactivity, and corrosivity, persons working with chemicals should be aware of those materials which fall into the following categories. These materials should be used in laboratory chemical hoods and in other areas that are considered "designated areas". These are areas where it is understood that materials of higher toxicity may be encountered. These materials must be stored in areas designated for "particularly hazardous substances."

a. OSHA select chemicals and carcinogens

A carcinogen is any substance or agent that is capable of causing cancer – the abnormal or uncontrolled growth of new cells in any part of the body in humans or animals. Carcinogens are chronic toxins with long latency periods that can cause damage after repeated or long duration exposures and often do not have immediate apparent harmful effects.

The OSHA Lab Safety Standard defines a "Select Carcinogen" as any substance, which meets one of the following criteria:

(i) It is regulated by OSHA as a carcinogen; or

(ii) It is listed under the category, "known to be carcinogens," in the Annual Report on Carcinogens published by the National Toxicology Program (NTP) (latest edition); or

(iii) It is listed under Group 1 ("carcinogenic to humans") by the International Agency for Research on Cancer Monographs (IARC) (latest editions); or

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

(A) After inhalation exposure of 6-7 hours per day, 5 days per week, for a significant portion of a lifetime to dosages of less than 10 mg/m(3);

(B) After repeated skin application of less than 300 (mg/kg of body weight) per week; or

(C) After oral dosages of less than 50 mg/kg of body weight per day.

With regard to mixtures, OSHA requires that a mixture, "shall be assumed to present a carcinogenic hazard if it contains a component in concentrations of **0.1% or greater**, which is considered to be carcinogenic.

The State of California has developed an extensive list of "Carcinogens Known to the State of California through Prop 65". Please note, this list is being provided as additional information and is not legally mandated by New York State.

Table 1: OSHA Select Carcinogens

Asbestos	N-Nitrosodimethylamine
4-Nitrobiphenyl	Vinyl Chloride
alpha-Naphthylamine	Inorganic Arsenic
Methyl chloromethyl ether	Cadmium
3,3'-Dichlorobenzidine	Benzene
bis-Chloromethyl ether	1,2-Dibromo-3-chloropropane
beta-Naphthylamine	Acrylonitrile
Benzidine	Ethylene oxide
4-Aminodiphenyl	Formaldehyde
Ethyleneimine	Methylenedianiline
beta-Propiolactone	1,3-Butadiene
2-Acetylaminofluorene	Methylene chloride
4-Dimethylaminoazobenzene	

Optional Modules:
OSHA Safety and Health Topics for Carcinogens webpage.

b. Reactives

Water Reactives and Pyrophorics

Water reactives are chemicals that react violently with water. They may release heat; release flammable, toxic, or oxidizing vapors; release metal oxide fumes; or form corrosive acids.

Examples: Alkali metals such as Sodium, Carbides such as calcium carbide, Anhydrides such as acetic anhydrides, and oxides such as sodium oxides.

Air and/or moisture reactive chemicals need to be stored and used under an inert environment (i.e. glove box). Specific protocols shall be developed and followed for proper storage and handling of air/moisture reactive chemicals.

Other chemicals may require specific use/storage conditions, such as pyrophorics or air reactive chemicals that need to be used/stored under inert atmosphere (e.g. nitrogen purge glove box). Always review MSDS for proper storage conditions.

c. **Acutely toxic chemicals**

Acute toxicity is the ability of a chemical to cause a harmful effect after a single exposure (e.g. potassium cyanide). 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 <200 mg (rabbits, per kg), inhalation LC50 of <200 (rats, ppm for 1 hr) or, <2000 (rats, mg/m^3 for 1 hr).

http://www.ncsu.edu/ehs/www99/right/handsMan/worker/toxic.htm

d. Reproductive Hazards

Through the course of work at NC State University, employees may work with agents, which are known or suspect to be hazardous to human reproduction. These agents include radiation, chemicals, biological agents, and physical hazards, as well as many other factors (standing, climbing, heat/cold exposure, medications, etc). Since risk factors are encountered both in work and at home, a review by the concerned employee's personal physician is recommended so that a complete picture can be obtained. .

Consultation is also available through the Environmental Health and Safety Center and NC consulting physicians associated with the University occupational medicine program.

The NC State Reproductive Health Program includes procedures and links to listings of chemicals suspected or known to cause reproductive effects in animals or humans. http://www.ncsu.edu/ehs/www99/right/handsMan/worker/REPRO_HEALTH_PROG.pdf

Optional Modules:
Duke University Particularly Hazardous Substances List

e. Highly Flammable

Chemicals requiring specific storage/use conditions:
Flammables that need to be kept refrigerated (based on MSDS) shall be kept in a "**flammable liquid storage refrigerator**". Unless used in an explosion-proof area, it is neither cost effective nor necessary to purchase an explosion-proof refrigerator.

f. Nano material

Engineered nanomaterials - Carbon nanotubes, carbon nanowires, carbon fullerenes, nanodots and any other material which has structured components with at least one dimension less than 100 nanometer, including carbon containing materials and other materials of differing elemental composition. These materials may be part of a liquid suspension or may be individual particles or fibers. This definition does not apply to engineered nanomaterials incorporated into a finished manufactured product, nor applies to ultra fine particles which occur in this size but are generated as products of combustion such welding fume or diesel exhaust.
http://www.ncsu.edu/ehs/nano/checklist.htm

g. Self polymerizing chemicals

Refers to a group of chemicals that create their own reaction when two or more small molecules (monomers) combine to form chains of repeating structures (polymers). When this reaction starts within the container of monomer, it can result in extremely high temperatures or pressures.

Examples: Acrylic acid, Styrene, and Vinyl Chloride, 1,3-Butadiene

h. **Selected Chemicals which pose a Skin Absorption Hazard**

Hazardous chemicals listed in the 2009, or most current, TLV (Threshold Limit Values) Booklet by the American Conference of Governmental Industrial Hygienists (ACGIH) as having a "potential significant contribution to the overall exposure by the cutaneous route, including mucous membranes and the eyes, either by contact with vapors, or, of probable greater significance, by direct skin contact with the substance."
http://www.ncsu.edu/ehs/www99/right/handsMan/lab/skin%20absorption.pdf

i. **Hydrofluoric acid** (Hydrogen fluoride, HF)

Hydrofluoric Acid (HF) is one of the strongest and most corrosive acids known. Therefore, special safety precautions are necessary when using this chemical. Anyone using HF should implement the following safety measures. Most importantly, do not assume that dilute solutions do not require special precautions!

- Read the Material Safety Data Sheet (MSDS) for the product or reagent that contains Hydrofluoric Acid. Be sure it is the MSDS for the specific formula you are using. Call the supplier for additional information if necessary.
- Be sure that you are using personal protective equipment that has been shown to effectively protect against Hydrofluoric Acid exposure. HF burns penetrate deeply into skin and muscle tissue and can't be treated by simply flushing the area with water.
- Make sure that you have Calcium gluconate gel available in your lab (contact student Health Pharmacy if you need calcium gluconate)
- Before using Hydrofluoric Acid, be sure you have a clear idea of what you will do in the event of a spill, skin exposure, eye exposure, etc. involving

Hydrofluoric Acid. **First aid and medical treatment for HF exposure is very specific and critical.** The special nature of the reaction of the fluoride ion with calcium in human tissue requires immediate action.

j. Perchloric Acid

Perchloric acid can be a health hazard if inhaled, ingested or splashed on skin or eyes. Once heated above room temperature or used at concentrations above 72% (any temperature), perchloric acid becomes a strong oxidizing acid. Organic materials are especially susceptible to spontaneous combustion if mixed or contacted with perchloric acid. Perchloric acid vapors may form shock sensitive perchlorates in ventilation system ductwork. Perchloric acid shall be used only in specially designed "perchloric acid" hood. For more information, see NC State University Guidelines for Perchloric Acid Use and Storage

k. **Peroxide forming chemicals**

Many organic chemicals used in laboratory solutions and reagents (e.g. ethyl ether) can form peroxide crystals, which can be extremely shock sensitive and have been known to cause explosions. Generally, the more volatile a compound, the greater its potential hazard, because evaporation significantly can increase peroxide concentration. Peroxide forming chemicals such as Ethyl Ether shall be dated as received, and discarded 12-month after opening. These chemicals shall never be kept and used beyond their expiration date.

http://www.ncsu.edu/ehs/www99/right/handsMan/lab/Peroxide.pdf

l. Picric acid (explosive)

Picric Acid is often found in science laboratories and is primarily used as a staining reagent and in synthesis reactions. Picric acid is a pale yellow, odorless crystal that is slightly soluble in water. The manufacturers usually distribute acid as a solution with greater than 10% water. As the water evaporates over time, the substance becomes dry picric acid crystals. Dry picric acid forms a very heat, shock and friction sensitive explosive crystal, especially when it is combined with **metals** such as copper, lead, zinc and iron. It will also react with **alkaline materials** including plaster and concrete to form explosive picrate salts, which are more reactive and shock sensitive than the acid itself.

14. **Emergency Procedures**

a. Spills

Small–scale hazardous material spills shall be cleaned only by trained and authorized employees who are well aware of the hazards and decontamination methods for the particular chemicals involved. The employee shall be fully prepared and equipped with proper personal protection equipment. For large-scale spills, evacuate the building and call 911. See the following links for detailed information:

http://www.ncsu.edu/ehs/spill.htm

http://www.ncsu.edu/ehs/www99/right/handsMan/factsheet/spills.pdf

b. Fire

- Activate fire alarm pull station if in a building.
- Immediately leave the building – and if possible
- Shut off equipment, stabilize experiments if you can quickly
- Close your door, and
- Alert others
- DO NOT USE ELEVATORS
- Assist others in evacuating if possible. Have those you cannot assist wait in areas designated RESCUE ASSISTANCE.
- Call Campus Police–
    - campus phone 911,
    - activate emergency blue light phone
- Assemble a safe place away from danger; account for others from your office, floor, etc.
- Person with knowledge of the situation should meet with first responders.
- Do not re-enter the building until cleared by first responders.

c. Medical Assistance

- Call Campus Police–
    - campus phone 911,
    - activate emergency blue light phone,

- **Stay on the phone** . You will be asked questions that the Communicator will provide to first responders.
- Do not move someone who is injured unless they are in danger.
- Keep the injured person comfortable until help arrives.
- Report job related injuries to the supervisor.

Minor Injuries – Employees

- Report the injury to your supervisor.

Note : Supervisors will follow the procedures for all accidents located at http://www.ncsu.edu/ehs/accidents/occacc1.htm

Minor Injuries – Students

- Students may call Student Health Services at 515-2563 for advice
- Students may call Campus police for an escort to or from Student Health Services (on campus only).

See EH&S website for additional information:

http://www.ncsu.edu/ehs/emerg_info.htm

For chemical spills affecting any part of the body see the following:

http://www.ncsu.edu/ehs/www99/right/handsMan/factsheet/Chemical%20Spills%20On%20Personnel.pdf

15. **Special Procedures**

a. Shipping of hazardous materials

The US Department of Transportation (DOT) and International Air Transporters Association (IATA) regulate all domestic and international hazardous material shipping. All persons shipping hazardous materials, or equipment containing hazardous materials, must be certified prior to offering these materials for shipment. NC State EHS offers certification classes for hazardous material shippers at no charge. For more information regarding the shipment of hazardous materials consult http://ncsu.edu/ehs/dot/ or contact Todd Becker at 919-515-2895 or todd_becker@ncsu.edu

b. Importing and development of new materials – TSCA

i. Chemicals developed in lab

Procedures for chemical substances developed in the laboratory

Planning a new experiment for new substance development will require a process hazard review of the PI.

The following provisions shall apply to chemical substances developed in the laboratory:

If the composition of the chemical substance that is produced exclusively for the laboratory's use is known, the PI/Supervisor shall determine if it is a hazardous chemical defined as a **chemical** for which there is statistically significant evidence based on at least one study conducted in accordance with established scientific principles that acute or chronic health effects may occur in exposed employees. The term "health hazard" includes chemicals which are carcinogens, toxic or highly toxic agents, reproductive toxins, irritants, corrosives, sensitizers, hepatotoxins, nephrotoxins, neurotoxins, agents which act on the hematopoietic systems, and agents which damage the lungs, skin, eyes, or mucous membranes. Appendices A and B of the Hazard Communication Standard (29 CFR 1910.1200) provide further guidance in defining the scope of health hazards and determining whether or not a **chemical** is to be considered hazardous.

If the chemical is determined to be hazardous, the PI shall provide appropriate training (see section 4) and implement CHP requirements. If the chemical produced is a byproduct whose composition is not known, the PI shall assume that the substance is hazardous (training and CHP requirements shall be implemented).

If the chemical substance is produced for another user outside of the laboratory, the PI shall comply with the Hazard Communication Standard (29 CFR 1910.1200) including the requirements for preparation of material safety data sheets and labeling.

c. Controlled Substances

Controlled substances are any drugs or chemical substances whose possession and use are regulated under the United States Controlled Substances Act, or the North Carolina Controlled Substances Act. The U.S. Department of Justice, Drug Enforcement Administration (DEA) administers the federal law, and the North Carolina Department of Health and Human Services, Drug Control Unit (NC-DCU) administers the state law. Controlled substances have stimulant, depressant, or hallucinogenic effects on the higher functions of the central nervous system, and tend to promote abuse or physiological/psychological dependence.

For more information please refer to NC State University's Controlled Substances Program NCSU Controlled Substance Program.

16. Hazardous Waste

The Environmental Health and Safety Center (EH&S) has implemented a comprehensive program for the management of hazardous materials and wastes from University operations. The EH&S manages programs for disposal of hazardous materials. Each user of a hazardous material should consider the hazards of the chemicals and gases they use, utilize the least hazardous material practicable, and consider strategies to minimize or eliminate hazardous waste.

Hazardous materials are considered components used in a potentially dangerous process, including storage, research, and maintenance activities. Those materials or components and their byproducts become a waste when removed from the process and intended for discard or determined to no longer be of use.

For NC State purposes, the term "hazardous materials" is intended to cover materials and wastes, including hazardous waste, low-level radioactive waste (LLRW), regulated and non-regulated biomedical waste, mixed waste (waste containing both chemicals and LLRW) and other waste that may require special disposal or handling procedures. For comprehensive Hazardous Waste program information, please consult the NC State Hazardous Waste Generators Manual

http://www.ncsu.edu/ehs/haz_waste/index.htm

i. Satellite accumulation

Wastes must be accumulated in the room where generated. Deviation from this requires review by EH&S. Accumulation requirements include appropriate containers properly marked and managed. Detailed information is provided in the NC State Hazardous Waste Generators Manual

ii. Drain disposal:

Many hazardous materials are regulated as hazardous wastes at concentrations of only a few parts per million. Many seemingly non-hazardous materials may impact biological treatment processes at a municipal wastewater treatment plant, or simply pass through the plant untreated. Most chemical wastes are not approved for drain disposal. Exceptions should be reviewed by EH&S.

iii. Waste Minimization

Each Principal Investigator is responsible for ensuring materials are properly used, stored, and disposed. He/She should purchase only what is needed, rotate or redistribute materials, and design procedures to minimize the generation of hazardous wastes.

17. **Physical hazards**

a. Compressed gases

Compressed gas cylinders can present a variety of hazards due to their pressure and /or contents. All compressed gases used at NC State University must be ordered through University Central stores.

http://www.ncsu.edu/ehs/www99/right/handsMan/compgas/compgas.html

Optional Modules:
Appendix VI, Compressed gas

b. Lasers – exclusion and pointer

Class 3B and 4 lasers can present a variety of hazards to both personnel operating the lasers and others through exposure to direct or reflected beams. Additional hazards such as exposure to high voltage power supplies, gas and vapor exposure, noise expo sure and fire hazards must also be considered and factored into laser lab designs and safe operating procedures. Please contact Environmental Health and Safety (EHSC) at 515-6860 for questions or comments.

http://www.ncsu.edu/ehs/www99/right/handsMan/lasers/laser.html

c. Noise and vibration

http://www.ncsu.edu/ehs/www99/right/handsMan/worker/hearing.html

d. UV link:

http://www.ncsu.edu/ehs/www99/right/handsMan/worker/uv.html

e. Cryogenic hazards

http://www.ncsu.edu/ehs/www99/right/handsMan/worker/Cryogenic_Safety.htm

18. Chemical Security (DHS)

The Department of Homeland Security (DHS) has issued Chemical Facility Anti-Terrorism Standards for any facility that manufactures, uses, stores, or distributes designated chemicals above a specified quantity.

All laboratory and non-laboratory facilities shall report (in their safety plans) the total quantity of the designated chemicals, listed by DHS. Any major change in the quantity of these chemicals (increase or decrease) or a new start up shall be reported to EH&S within 30 days.

http://www.dhs.gov/xlibrary/assets/chemsec_appendixa-chemicalofinterestlist.pdf

19. Recordkeeping

Where medical exams are provided, University Health will establish and maintain for each employee an accurate record of medical consultation and examinations including tests or written opinions required by OSHA. EH & S will maintain an accurate record of any measurements taken to monitor employee exposure to hazardous materials.

20. Additional References/supporting programs/documents/links

a. Lab safety manual

http://www.ncsu.edu/ehs/lab.htm

b. Health and Safety manual

http://www.ncsu.edu/ehs/healthsafety_man.htm

c. Single page fact sheet

http://www.ncsu.edu/ehs/www99/right/handsMan/factsheet/index.html

d. MSDS and International Cards

Appendix I

Corrosives

General Information

Corrosive materials are generally considered to be chemicals that cause chemical burns to the skin, such as strong acids or bases. Many corrosives are corrosive only because they readily react with water to produce an acid.

While skin contact with corrosives causes chemical burns, inhalation or ingestion of corrosive materials could be even more harmful. The lungs especially can be severely damaged by corrosive materials.

Handling Requirements

- Work only with materials after having examined their MSDS to consider their flammability, reactivity, corrosiveness, and toxicity.

Suitable gloves must be worn when handling any corrosive. An apron is advisable while handling bromine and hydrofluoric acid.

When handling any concentrated acid or strongly basic solution, a face shield or goggles must be worn. A fume hood sash may be used in place of a face shield or goggles provided that the glass of the sash is between the work and your face, and you do not have to assume an awkward body position.

All chemicals must be transported in a plastic bucket or other unbreakable secondary container, regardless of the size or composition of the primary container. If a cart with sides is used, no bucket is necessary.

Handling Guidelines

Avoid inhalation. All operations should be performed in a ventilated enclosure.

The recommended safety additional apparel for the handling of any highly corrosive materials includes: goggles or safety glasses and a face shield, gloves, gauntlets, and acid apron.

Appendix II
Reactive Materials

I. Introduction

The reactivity of any given chemical substance is a characteristic that is strongly influenced by several factors, including the nature of the co-reactant, impurities, catalysts, heat, light, pressure, etc.

Reactive liquids are chemicals that react vigorously with moisture or oxygen or other substances. Reactive solids are chemicals that react vigorously with moisture and other substances. The most common reactive solids include sodium, potassium and lithium metals, acid anhydrides and acid chlorides.

The reactivity of organic compounds may be correlated from a "functional group" point of view (e.g., alcohols, alkyl halides, amines, etc.)

The reactivity of inorganic compounds may be frequently correlated with their "family" in the periodic table. Within a given family, similar types of behavior are observed with changes in the magnitude of reactivity varying consistently with atomic weight. The reactivity of chemical compounds shows a similar correlation for a given class of compounds (e.g., the behavior of the hydrogen halides).

II. Handling Requirements

- Work only with materials after having examined their MSDS to consider their flammability, reactivity, corrosivity, and toxicity.
- Never combine chemicals indiscriminately.
- Materials labeled pyrophoric must be handled in an inert atmosphere.
- Quench alkali metal and metal hydride containing chemical reactions with an appropriate alcohol prior to adding water.
- Do not combine nitric acid in unfamiliar combinations with organic compounds.
- Never allow hydrogenation catalysts to become completely dry during laboratory operations.
- Always add acid to water, never water to acid.
- All chemical must be transported in a plastic bucket or other unbreakable secondary container, regardless of the size or composition of the primary container. If a cart with sides is used, no bucket is necessary.

III. Handling Guidelines

- Reactive chemicals should be used in a properly ventilated enclosure.
- Unfamiliar chemical combinations should be treated as if the potential for explosion exists. Use a blast shield and try the reaction on a very small scale the first time.
- Only clean glassware should be used.
- Use caution in cleaning laboratory equipment, which may contain reaction residues.
- Be aware of the potential for delayed or accelerating chemical reactions.
- Check all ethers for the presence of peroxides as appropriate.
- Add strong acids or bases very cautiously to any organic substrate.

Appendix III
Particularly Hazardous Materials (PHM)

I. Introduction

Particularly Hazardous Materials (PHMs) refers to chemicals in which there is statistically significant evidence based on one or more scientific studies that acute or chronic health effects may occur in exposed employees. This term includes chemicals which are carcinogens, toxic or highly toxic agents, reproductive toxins, irritants, corrosives, sensitizers, hepatotoxins, nephrotoxins, neurotoxins, agents which act on the hematopoietic system, and agents which damage the lungs, skin, eyes, or mucous membranes.

For many toxic materials, hygienic standards and recommendations have been established and action must be taken to prevent personnel from receiving exposures in excess of these levels. The recommendations may be referred to as threshold limit values (TLVs); standards may be referred to as permissible exposure limits (PELs). The MSDS (http://www.ncsu.edu/ehs/MSDS.htm) will list the hygienic standard and/or recommendation for the hazardous chemical or each component of a mixture. In addition, EHSC has a complete listing of published TLVs and PELs and other works concerning the subject of industrial toxicology.

Protection from PHMs is provided by ensuring that exposure to such hazards is minimized or eliminated. To minimize the exposure, it is necessary to determine the route by which the exposure may occur, i.e. inhalation, skin contact, puncture, ingestion, or a combination of exposure routes.

II. Handling Requirements

- Work only with materials after having examined their MSDS to consider their flammability, reactivity, corrosivity, and toxicity.
- An area must be designated for work involving PHMs. It may be a ventilated enclosure (e.g., fume hood, biosafety cabinet, balance enclosure, or glove box), or a portion of a laboratory. The "designated area" must be specifically marked.
- Personnel trained to work with PHMs should only work with those chemicals in the "designated areas".
- Determine the appropriate decontamination procedure before work is started.
- All chemical must be transported in a plastic bucket or other unbreakable secondary container, regardless of the size or composition of the primary container. If a cart with sides is used, no bucket is necessary.
- PHM samples that are "dry" must be restricted to a ventilated enclosure or other designated area. This includes dry compound operations, such as grinding, pressing, etc., which would create airborne dust contamination.
- If a PHM is spilled, it must be cleaned up following appropriate procedures and disposed of accordingly.

III. Handling Guidelines

- **Allergens**
  - Examples: diazomethane, isocyanates, bichromates
  - Wear suitable gloves to prevent hand contact with allergens or substances of unknown allergenic activity.
  - Conduct aerosol-producing procedures in a fume hood.
- **Embryo toxins/Reproductive Toxins**
  - Examples: organomercurials, lead compounds, formamide
  - Women of childbearing potential should handles these substances only in a fume hood whose proper performance has been confirmed, using

    appropriate protective apparel (especially gloves) to prevent skin contact.
  - Review each use of these materials with the principle investigator and review continuing uses annually.
  - Store embryo toxins and reproductive toxins in unbreakable containers or unbreakable secondary containers in a well-ventilated area.
  - Notify supervisors and EHSC of all incidents of exposure or spills; EHSC will arrange for a medical consolation when appropriate.
- **Chemicals of Moderate Chronic or High Acute Toxicity**
  - Examples: diisopropylfluorophosphate, hydrofluoric acid, hydrogen cyanide
  - Follow the specific precautions and procedures for the chemical.
  - Use and store these substances only in designated (restricted access) areas with appropriate warning signs.
  - Use a fume hood or other containment device for procedures which may result in the generation of aerosols or vapors; trap released vapors to prevent their discharge with fume hood exhaust.
  - Avoid skin contact by use of suitable gloves and long sleeves and other protective apparel as appropriate.
  - Maintain records of the amounts of materials on hand, amounts used, and the names of the lab workers involved.
  - Be prepared for accidents and spills. At least two people should be present at all times if compounds in use are highly toxic or of unknown toxicity.
  - Store breakable containers in chemically resistant trays; also work and mount apparatus above such trays or cover work and storage surfaces with removable, absorbent, plastic backed paper.
  - If a major spill occurs outside the hood, evacuate the area and call for assistance.
  - Thoroughly decontaminate or dispose of contaminated clothing or shoes. If possible, chemically decontaminate by chemical conversion to a less toxic product.
  - Store contaminated waste in closed, suitably labeled, impervious containers.

- **Chemicals of High Chronic Toxicity**
  - Examples: dimethylmercury, nickel carbonyl, benzo-a-pyrene, N-nitrosodiethylamine, other human carcinogens or substances with high carcinogenic potency in animals
  - Conduct all transfers and work in designated (restricted access) areas: a restricted access hood, glove box, or portion of a lab, designated for use of highly toxic substances, for which all persons with access are aware of the substances being used and necessary precautions.
  - Protect vacuum pumps against contamination with scrubbers or HEPA filters and vent effluent into the hood.
  - Decontaminate vacuum pumps or other contaminated equipment, including glassware, before removing them from the designated area. Decontaminate the designated area before normal work is resumed there.
  - On leaving the area, remove protective apparel (placing it in an appropriate, labeled container) and thoroughly wash hands, forearms, face, and neck.
  - Use a wet mop or a vacuum cleaner equipped with a HEPA filter to decontaminate surfaces. DO NOT DRY SWEEP SPILLED POWDERS.
  - If using toxicologically significant quantities of a substance on a regular basis (in quantities above a few milligrams to a few grams, depending on the substance, 3 or more times per week), contact EHSC. EHSC will arrange for a medical consultation, if appropriate.
  - Keep accurate records of the amounts of these substances stored and used, the dates of use, and names of users.
  - The designated area must be conspicuously marked with warning and restricted access signs and all containers should be appropriately labeled with identity and warning labels (e.g., CANCER-SUSPECT AGENT).
  - Ensure that contingency plans, equipment, and materials to minimize exposures of people and property in case of accident are available.
  - For a negative pressure glove box, ventilation rate must be at least 2-volume changes/hour and at a pressure of at least 0.5 inches of water gauge. For a positive pressure glove box, thoroughly test for leaks before each use. In either case, trap the exit gases or filter them through a HEPA filter and then release them into a fume hood.
  - Use chemical decontamination whenever possible; ensure that containers of contaminated wasted are transferred from the designated area under the supervision of authorized personnel.
- **Animal Work with Chemicals of High Chronic Toxicity**
  - For large-scale activities, special facilities with restricted access are preferable.
  - When possible, administer the substance by injection or gavage instead of in diet. If administration is in the diet, use a caging system under

negative pressure or under laminar airflow directed through HEPA filters prior to discharge.

- Devise procedures, which minimize formation and dispersal of contaminated aerosols, including those from food, urine, and feces (e.g., use HEPA filtered vacuum equipment for cleaning; moisten contaminated bedding before removal from the cage; mix diets in closed containers in a hood).
- When working in the animal room, wear plastic or rubber gloves, fully buttoned laboratory coat or jumpsuit and, if needed because of incomplete suppression of aerosols, other apparel and equipment (shoe and head coverings, respirator).
- Dispose of contaminated animal tissues and excreta using approved methods.

Appendix IV
Chemical Toxicology

Introduction

Toxicology is the study of the nature and action of poisons. Toxicity is the ability of a chemical molecule or compound to produce injury once it reaches a susceptible site in or on the body. Toxicity hazard is the probability that injury will occur considering the manner in which the substance is used.

Dose-Response Relationships

The potential toxicity (harmful action) inherent in a substance is manifest only when that substance comes in contact with a living biological system. A chemical normally thought of as "harmless" will evoke a toxic response if added to a biological system in sufficient amount. The toxic potency of a chemical is defined by the relationship between the dose (the amount) of the chemical and the response that is produced in a biological system.

Routes of Entry into the Body

There are four main routes by which hazardous chemicals enter the body:

- Inhalation: Absorption through the respiratory tract. Most important in terms of severity.
- Skin absorption.
- Ingestion: Absorption through the digestive tract. Can occur through eating or smoking with contaminated hands or in contaminated work areas.
- Injection. Can occur by accidental needle stick or puncture of skin with a sharp object.

Most exposure standards, Threshold Limit Values (TLVs) and Permissible Exposure Limits (PELs), are based on the inhalation route of exposure. They are normally expressed in terms of either parts per million (ppm) or milligrams per cubic meter (mg/m^3) concentration in air.

If a significant route of exposure for a substance is through skin contact, the TLV or PEL will have a "skin" notation. Examples are pesticides, carbon disulfide, carbon tetrachloride, dioxane, mercury, thallium compounds, xylene, and hydrogen cyanide.

Types of Health Effects

Acute poisoning is characterized by rapid absorption of the substance and the exposure is sudden and severe. Normally, a single large exposure is involved. Examples are carbon monoxide or cyanide poisoning.

Chronic poisoning is characterized by prolonged or repeated exposures of a duration measured in days, months or years. Symptoms may not be immediately apparent. Examples are lead or mercury poisoning, pesticide exposure.

Local refers to the site of action of an agent and means the action takes place at the point or area of contact. The site may be skin, mucous membranes, the respiratory tract, gastrointestinal system, eyes, etc. Absorption does not necessarily occur. Examples are strong acids or alkalis and war gases.

Systemic refers to a site of action other than the point of contact and presupposes absorption has taken place. For example, an inhaled material may act on the liver. Examples are arsenic affects the blood, nervous system, liver, kidneys and skin; benzene affects bone marrow.

Materials that tend to build up in the body as a result of numerous chronic exposures characterize cumulative poisons. The effects are not seen until a critical body burden is reached. Examples are heavy metals.

Substances in combination, meaning two or more hazardous materials present at the same time whose resulting effect is greater than the effect predicted based on the individual substances. This combined effect is called a **synergistic** or **potentiating** effect. An example is exposure to alcohol and chlorinated solvents.

Other Factors Affecting Toxicity

- Rate of entry and route of exposure; that is, how fast the toxic dose is delivered and by what means.
- Age can affect the capacity to repair tissue damaged.
- Previous exposure can lead to tolerance, increased sensitivity, or make no difference.
- State of health, medications, physical condition, and life style can affect the toxic response. Pre-existing disease can result in increased sensitivity.
- Environmental factors, such as temperature and pressure.
- Host factors, including genetic predisposition and the sex of the exposed individual.

Physical Classifications of Toxic Materials

Gas applies to a substance, which is in the gaseous state at room temperature and pressure.

A **vapor** is the gaseous phase of a material, which is ordinarily a solid or a liquid at room temperature and pressure.

When considering the toxicity of gases and vapors, the **solubility** of the substance is a key factor. Highly soluble materials like ammonia irritate the upper respiratory tract. On the other hand, relatively insoluble materials like nitrogen dioxide penetrate deep into the lung. Fat-soluble materials, like pesticides, tend to have longer residence times in the body.

An **aerosol** is composed of solid or liquid particles of microscopic size dispersed in a gaseous medium. The toxic potential of an aerosol is only partially described by its concentration in milligrams per cubic meter (mg/m^3). For a proper assessment of the toxic hazard, the size of the aerosol's particles is important. Particles above 1 micrometer tend to deposit in the upper respiratory tract. Below 1-micrometer particles enter the lung. Very small particles (< 0.2 um) are generally not deposited.

Physiological Classifications of Toxic Materials

Irritants are materials that cause inflammation of mucous membranes with which they come in contact. Inflammation of tissue results from concentrations far below those needed to cause corrosion. Examples include:

- ammonia
- hydrogen chloride
- halogens
- phosgene
- nitrogen dioxide
- arsenic trichloride
- phosphorus chlorides
- alkaline dusts and mists
- diethyl/dimethyl sulfate
- hydrogen fluoride
- ozone

Irritants can also cause changes in the mechanics of respiration and lung function. Examples include:

- sulfur dioxide
- formaldehyde
- sulfuric acid
- iodine
- acetic acid
- formic acid
- acrolein

Long-term exposure to irritants can result in increased mucous secretions and chronic bronchitis.

A **primary irritant** exerts no systemic toxic action either because the products formed on the tissue of the respiratory tract are non-toxic or because the irritant action is far in excess of any systemic toxic action. Example: hydrogen chloride.

A **secondary irritant's** effect on mucous membranes is over-shadowed by a systemic effect resulting from absorption. Examples include hydrogen sulfide and aromatic hydrocarbons.

Exposure to a secondary irritant can result in pulmonary edema, hemorrhage, and tissue necrosis.

Corrosives are chemicals, which may cause visible destruction or irreversible alterations in living tissue by chemical action at the site of contact. Examples include sulfuric acid, potassium hydroxide, chromic acid, and sodium hydroxide

Asphyxiants have the ability to deprive tissue of oxygen.

> **Simple asphyxiants** are inert gases that displace oxygen. Examples include, nitrogen. nitrous oxide, carbon dioxide, hydrogen, and helium.
> **Chemical asphyxiants** have as their specific toxic action rendering the body incapable of utilizing an adequate oxygen supply. They are toxic at very low concentrations (few ppm). Examples include carbon monoxide and hydrogen cyanide.

Primary anesthetics have a depressant effect upon the central nervous system, particularly the brain. Examples include halogenated hydrocarbons, ether, and alcohols.

Hepatotoxic agents cause damage to the liver. Examples include carbon tetrachloride, nitrosamines, and tetrachloroethane.

Nephrotoxic agents damage the kidneys. Examples include halogenated hydrocarbons and uranium compounds.

Neurotoxin agents damage the nervous system. The nervous system is especially sensitive to organometallic compounds and certain sulfide compounds. Examples include:

- trialkyl tin compounds
- methyl mercury
- organic phosphorus
- insecticides
- tetraethyl lead
- carbon disulfide
- thallium
- manganese

Some toxic agents act on the blood or hematopoietic system. The blood cells can be directly affected or bone marrow can be damaged. Examples include:

- nitrites
- toluidine
- benzene
- aniline
- nitrobenzene

There are toxic agents that produce damage of the pulmonary tissue (lungs) but not by immediate irritant action. Fibrotic changes can be caused by free crystalline silica and asbestos. Other dusts can cause a restrictive disease called pneumoconiosis. Examples include coal dust, cotton dust and wood dusts.

A **carcinogen** commonly describes any agent or mixture, which contains an agent that can initiate or speed the development of malignant or potentially malignant tumors or malignant neoplastic proliferation of cells. Known human carcinogens include:

- asbestos
- alpha-napthylamine
- 3,3'-dichlorobenzidine
- vinyl chloride
- ethylene oxide
- N-nitrosodimethylamine
- inorganic arsenic
- 1,2-dibromo-3-chloropropane (DBCP)
- coal tar pitch volatiles
- 4-nitrobiphenyl
- methyl chloromethyl ether
- bis-chloromethyl ether

A **mutagen** affects the chromosome chains of exposed cells. The effect is hereditary and becomes part of the genetic pool passed on to future generations.

A **teratogen** (embryo toxic or fetotoxic agent) is an agent, which interferes with normal embryonic development without damage to the mother or lethal effect on the fetus. Effects are not hereditary. Examples include lead and dibromodichloropropane.

A **sensitizer** causes a substantial proportion of exposed people to develop an allergic reaction in normal tissue after repeated exposure to the chemical. The reaction may be as mild as a rash (contact dermatitis) or as serious as anaphylactic shock. Examples include:

- epoxides
- amines
- poison ivy
- toluene diisocyanate
- chromium compounds
- chlorinated hydrocarbons
- formaldehyde
- nickel compounds

<u>Target Organ Effects</u>

The following is a target organ categorization of effects, which may occur, including examples of signs and symptoms and chemicals, which have been found to cause such effects.

- **Hepatotoxics cause liver damage**
  Signs and symptoms: jaundice, liver enlargement

Example chemicals:	carbon tetrachloride, nitrosamines, chloroform, toluene, perchloroethylene, cresol, dimethylsulfate

- **Nephrotoxics produce kidney damage**

Signs and symptoms:	edema, proteinuria
Example chemicals:	halogenated hydrocarbons, uranium, chloroform, mercury, dimethyl sulfate

- **Neurotoxins affect the nervous system**

Signs and symptoms:	narcosis, behavioral changes, decreased muscle coordination
Example chemicals:	mercury, carbon disulfide, benzene, carbon tetrachloride, lead, mercury, nitrobenzene

- **Hematopoietic agents decrease blood functions**

Signs and symptoms:	cyanosis, loss of consciousness.
Example chemicals:	carbon monoxide, cyanides, nitrobenzene, aniline, arsenic, benzene, toluene

- **Pulmonary agents irritate or damage the lungs**

Signs and symptoms:	cough, tightness in chest, shortness of breath.
Example chemicals:	silica, asbestos, nitrogen dioxide, ozone, hydrogen sulfide, chromium, nickel, alcohol.

- **Reproductive toxins affect the reproductive system. (mutations and teratogenesis)**

Signs and symptoms:	birth defects, sterility.
Example chemicals:	lead, dibromodichloropropane.

- **Skin hazards affect the dermal layer of the body**

Signs and symptoms:	Skin rashes, irritation.
Example chemicals:	ketones, chlorinated compounds, alcohols, nickel, phenol, trichloroethylene.

- **Eye hazards affect the eye or vision**

Signs and symptoms:	conjunctivitis, corneal damage.
Example chemicals:	organic solvents, acids, cresol, quinone, hydroquinone, benzyl chloride, butyl alcohol, bases.

Appendix V
Explosives

General Information

Explosives are compounds that are unstable under a given set of conditions. Their instability can be caused by an extreme sensitivity to heat, shock, sparks, or other forms of detonation. TNT and nitroglycerin are commonly known primary explosives. A lesser-known class, called low-power explosives, contains organic peroxides and peracids that are routinely used in laboratories.

Peroxides are among the most hazardous chemicals normally handled in laboratories. Many peroxides are far more sensitive to shock than most primary explosives. They have a specific half-life or rate of decomposition that may auto-accelerate into a violent explosion, especially in bulk quantities. Peroxides are sensitive to heat, friction, impact, and light as well as to strong oxidizing and reducing agents. All organic peroxides are extremely flammable. Fires involving bulk quantities of peroxides should be approached with extreme caution.

Under certain conditions, compounds such as tetrohydrofuran (THF) and diethyl ether will form peroxides. These compounds must be handled with the same caution and safety as peroxides. For storage purposes, stabilizers are commonly added to peroxides or peroxide forming compounds.

Peracids may also be classified as explosive. For example, aqueous solutions of perchloric acid up to concentrations of 60-70% are quite stable thermally. The acid is unstable and unsafe to use and handle in concentrations above 60-70%. It is a powerful oxidizing agent and serious explosions may occur when concentrated solutions are heated with substances that are easily oxidized. Perchloric acid is a very weak oxidizing agent when cold and dilute.

Handling Requirements

- Work only with materials after having examined their MSDS to consider their flammability, reactivity, corrosivity, and toxicity.
- Wear appropriate PPE.
- Do not return unused peroxides to the original container.
- The sensitivity of most peroxides to shock and heat can be reduced by dilution with inert solvent such as aliphatic hydrocarbons.
- Do not use solutions of peroxides in volatile solvents under conditions in which all the solvent will be vaporized, thereby increasing the peroxide concentration in the solution.
- Never use a metal spatula with peroxides since contamination by metals can lead to explosive compositions. Use ceramic or wooden spatulas.
- Open flames or other sources of heat should not be permitted near peroxides.

- Avoid friction, grinding, and all forms of impact, especially with solid peroxides. Glass containers with screw-cap lids or glass stoppers should not be used. Use polyethylene bottles with screw-cap lids.
- Peroxides should be stored at the lowest possible temperature consistent with solubility or freezing points to minimize the rate of decomposition. Do not refrigerate liquid or solutions of peroxide at or below the temperature at which the peroxide freezes or precipitates. Peroxides in these forms are sensitive to shock and heat.
- Containers of ethers must be labeled with the date they are opened, and the contents should be destroyed by the user within three months.
- Chemicals that are known to form peroxides upon long exposure to air must be sealed tightly.
- All chemicals must be transported in a plastic bucket or other unbreakable secondary container, regardless of the size or composition of the primary container. If a cart with sides is used, no bucket is necessary.

Handling Guidelines

- When handling peroxides, a face shield or goggles should be worn. A fume hood door may be used in place of a face shield or goggles provided that the glass of the sash is between the work and your face, and you do not have to assume an awkward body position.
- Peroxides should be handled in a fume hood. The quantity of peroxide to be handled should be limited to the minimum amount required.

Appendix VI
Compressed Gas

Compressed Gases

General Information

Gases are compressed up to 3000-psi pressure and any sudden release of pressure may cause serious harm to personnel and major damage to equipment. When working with any compressed gas, the gas pressure in the cylinder is always a safety hazard to be considered.

Liquefied gases have very low boiling points and are stored as liquids in pressurized cylinders. Contact with these materials either directly or through non-insulated containers may cause 'burns' due to freezing of skin tissue.

The handling of compressed gases must be considered more hazardous than the handling of liquid or solid material in a normal state. This is due to the following properties unique to compressed gases: pressure, diffusion, low flash points for many flammable gases, low boiling points, and limited visual and/or odor detection.

Hazards may also arise from equipment failure and leakage from systems that are not pressure tight. Improper pressure control may cause unsafe reaction rates due to poor flow control. Diffusion of leaking gases may cause rapid contamination of the atmosphere, giving rise to toxic effects such as anesthesia, asphyxiation, and the rapid formation of explosive concentrations of flammable gases. The flash point of a flammable gas under pressure is always lower than ambient or room temperature. Therefore, leaking gas can rapidly form an explosive mixture with air.

Classifications

Gaseous and liquefied compressed gases may be categorized in the following classifications:

A. Corrosive
   Corrosives are those products that may erode and deteriorate materials that they contact, such as metals, fabrics, or human tissue. Some gases, although not corrosive in anhydrous form, become corrosive in the presence of water.
B. Flammable
   When mixed with air or other contaminants, a flammable gas will burn or explode upon ignition, depending on the degree of confinement.
C. Inert
   At ordinary temperatures and pressures, inert gases do not react with other materials. If released in a confined area, inert gases may displace the oxygen in the air below the level necessary to sustain life.
D. Oxidant

Although non-flammable, an oxidant gas may initiate and support combustion. All possible sources of ignition must be eliminated when handling oxidant gases.

E. Toxic

Toxic gases may produce harmful or lethal effects. The degree of toxicity varies with the gas. Some gases are particularly noxious because of limited visual and/or odor detection at low concentrations. Some gases are non-toxic themselves, but may react with certain chemicals to produce toxic materials.

Handling Requirements

- Work only with materials after having examined their MSDS to consider their flammability, reactivity, corrosiveness, and toxicity.
- Know and understand the physical properties of the gas.
- Never use a cylinder that cannot be positively identified.
- Transport compressed gas cylinders using a suitable hand truck with a chain or other mechanism to secure the cylinder. Valve protection cap must be in place. Small cylinders or lecture bottles should be transported using a suitable carrier. Do not drag, roll, or slide cylinders even for short distances.
- Never drop cylinders or permit them to strike each other violently.
- Protect cylinders from mechanical damage. Use a chain or web strap and eyebolts attached to a stationary object.
- Lecture bottles must be placed in a suitable stand or clamped while in use.
- Valve protection caps must always be in place except when cylinders are connected for use.
- Never lubricate, modify, force, or tamper with a cylinder valve. When not in use, cylinder valves should be tightly closed.
- Always wear industrial safety glasses when handling and using compressed gases.
- Do not extinguish a flame involving a highly combustible gas until the source of the gas has been shut off. It can again ignite causing an explosion.
- Never feed a compressed gas directly to a reaction vessel. A suitable trap must be used to avoid reaction solution from being drawn into the cylinder.
- Lines from the regulator to the delivery point must be compatible with the gas being used and must be checked before every use for cracks and leaks.
- A proper regulator must always be used to control the pressure of gas leaving the cylinder. A needle valve can be used to adjust the flow of gas into a reaction vessel. Additional valves may be required at the use point to control flow for specific operations. Lecture bottle cylinders may be controlled by a hand valve.
- Never bleed any cylinder completely empty. Leave a slight pressure to keep contaminants out. Tightly close the cylinder valve to avoid back siphoning or air or moisture into the cylinder.

- If a cylinder has a bad valve or is defective in another manner, write the situation on the label.

Handling Guidelines

- Consider using the minimum sized compressed gas cylinder required to perform an experiment.
- Empty cylinders should be returned to the storage area provided for empty cylinders.
- Promptly remove the regulator or valve from an empty cylinder and replace with the valve protection cap. The tag on the cylinder should be marked “empty” before returning it to the storage area.

Regulator Requirements

- Select a suitable regulator to use with each compressed gas cylinder. The regulator must be compatible with the gas and designed for the pressure in the cylinder. The high pressure gauge must never be pegged at its maximum reading. This condition indicates the wrong regulator has been selected.
- A clean, dry regulator should be attached to a cylinder. Force must not be used to connect fittings to a cylinder. Do not use pipe adapters to connect a regulator to a cylinder. A poor fit may indicate that the regulator chosen is not intended for use with the cylinder’s content.