THE UNIVERSITY OF RHODE ISLAND

Laboratory Chemical Hygiene Plan

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University of Rhode Island Laboratory Chemical Hygiene Plan

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University of Rhode Laboratory Chemical Hygiene Plan

Chapter 1.0 Chemical Hygiene Plan Overview

The purpose of the University of Rhode Island's Laboratory Chemical Hygiene Plan is to assist lab workers in conducting their research in a safe and productive manner. It provides an institutional model to assure consistent practices for handling, containing, and storing used and unused chemicals.

1.1 Introduction

The Occupational Safety and Health Administration's (OSHA) laboratory health standard, 29 CFR 1910.1450 "Occupational Exposures to Hazardous Chemicals in Laboratories" requires employers to implement exposure control programs and convey chemical health and safety information to laboratory employees working with hazardous materials. The full standard can be found at this link: <u>https://www.osha.gov/laws-regs/regulations/standardnumber/1910/1910.1450</u> Specific provisions of the standard require:

- Standard operating procedures involving the use of hazardous chemicals
- Criteria to determine and implement control measures to reduce employee exposure to hazardous chemicals
- Requirements to ensure that control measures perform properly
- Employee information and training
- Identification of operations requiring prior employer approval
- Medical consultation and examinations
- Designation of laboratory chemical hygiene officers
- Requirements for handling particularly hazardous chemicals
- Identification of designated areas (laboratories, storage rooms, disposal areas)
- Containment equipment
- Procedures for safe removal of contaminated waste
- Decontamination procedures

The standard operating procedures, laboratory practices, administrative, and engineering controls, outlined in this Chemical Hygiene Plan (CHP) identify the safeguards to be used when working with hazardous materials. This document is the generic plan for all laboratories at the University. These safeguards have been developed to protect laboratory workers from unsafe conditions in the vast majority of situations. There are instances, however, when the physical and chemical properties, the proposed use, the quantity used for a particular purpose, or the toxicity of a substance will be such that additional controls may be required to protect the laboratory worker. Professional judgment is essential in the interpretation of these standard operating procedures, and individual laboratories should modify these procedures to meet their specific uses and operational needs. However, these modifications must be in writing and maintained with the laboratory copy of this plan. The University of Rhode Island's Environmental Health and Safety Department (EH&S) shall be informed, in writing, of these changes. **The Principal Investigator/Laboratory Supervisor is responsible for writing the Laboratory-Specific Standard Operating Procedures for each laboratory, for training employees and students in that laboratory on those SOPs and documenting their training.**

The manner in which the University of Rhode Island is complying with each of the elements in OSHA's Laboratory Standard is detailed in this Chemical Hygiene Plan. The official copy of the University of Rhode Island Chemical Hygiene Plan is located at EH&S, 177 Plains Road and on the EH&S web site: <u>https://web.uri.edu/EH&S</u>.

1.2 Chemical Hygiene Responsibilities

The following positions assume direct responsibility for safety in the laboratory:

- **Department of Environmental Health and Safety (EH&S)** has the responsibility for performing laboratory inspections, developing tools to provide assistance in implementing the URI Chemical Hygiene Plan, annual training, reviewing, and updating the Plan.
- **College Dean** has the responsibility to ensure compliance with the University Chemical Hygiene Plan within the departments of his/her college.
- **Department Chair or Director of an administrative unit** is responsible for chemical hygiene in the department/unit. The Departmental Chair will function as the **departmental chemical hygiene officer** unless another individual is designated this responsibility and EH&S has been notified of this designation.
- **Principal Investigator (PI)** has the primary responsibility for chemical hygiene in their assigned laboratory/laboratories. He/she is responsible for:
 - Conducting workplace hazard assessments as needed and correcting unsafe practices noted in the assessments;
 - Following the URI Chemical Hygiene Plan by selecting and employing prudent laboratory practices, personal protective equipment (PPE) and engineering controls that reduce the potential for exposure to hazardous chemicals to below acceptable OSHA, NIOSH, and/or ACGIH standards;
 - Writing Laboratory-Specific Standard Operating Procedures (SOPs) that document the procedures for working safely with hazardous chemicals, hazardous drugs (including chemotherapy drugs), carcinogens, reproductive hazards, hazardous processes and equipment as defined in this Chemical Hygiene Plan. The situations that require prior approval by the Department Chair and/or EH&S must also be documented. These SOPs shall be maintained in the lab and updated when there is a change in procedures, chemicals and/or equipment.
 - Informing employees/students working in his/her laboratory of the hazards associated with the use of chemicals in the laboratory and instructing them in the safe laboratory practices, adequate controls, and procedures for dealing with accidents involving hazardous chemicals;
 - Ensuring that training for all laboratory members, including themselves, is up to date;
 - Assuring that all containers of chemicals are appropriately labeled and that labels on incoming containers are not defaced;
 - Maintaining copies of Safety Data Sheets that are received with orders of chemicals;
 - Maintaining an accurate and up-to-date chemical inventory and using the inventory to identify those chemicals that meet the definition of carcinogens, hazardous drugs, reproductive toxins, and acutely hazardous chemicals and designating areas for their appropriate use;
 - Supervising the performance of their staff to ensure the required chemical hygiene rules are adhered to in the laboratory;

- Ensuring that all laboratory deficiencies discovered and reported during EH&S's laboratory inspections are corrected in a timely manner and that those corrections are documented;
- Ensuring that appropriate controls (administrative and engineering controls and personal protective equipment) are available in the laboratory, that they are used, and are in good working order, and display a current certification sticker (in the case of a hood and BSC);
- Ensuring that safety equipment, such as spill kits, fire protection equipment, safety eyewash and shower stations and wall mounted oxygen and other gas sensors are available, unobstructed, maintained and calibrated (if required) and in proper working condition.
- Managing hazardous waste correctly to meet State and Federal hazardous waste requirements.
- Laboratory Personnel (includes students who are working in a laboratory), are responsible for:
 - Being aware of the hazards of the materials they are around or working with, and handling those chemicals in a safe manner;
 - Reviewing URI's Chemical Hygiene Plan and adhering to its policies and procedures;
 - Developing good chemical hygiene habits (i.e. chemical safety practices and procedures);
 - Scheduling laboratory experiments when the Principal Investigator or other responsible laboratory personnel are available so that students and staff are not working alone;
 - Reporting unsafe conditions to the principal investigator, immediate laboratory supervisor, and/or EH&S;
 - Ensuring that chemicals are properly segregated and placed in corrosive or flammable cabinets, glove boxes or other appropriate storage enclosures;
 - Maintaining cleanliness and proper housekeeping within the laboratory;
 - Informing EH&S when hazardous waste and biological waste is ready to be picked up from the laboratory for disposal;
 - The Principal Investigator and laboratory workers share responsibility for collecting, labeling and storing chemical hazardous waste properly, as well as informing visitors entering their laboratory of the potential hazards and safety rules/precautions to be followed while in the lab.
- Chemical Hygiene Officer has the responsibility for:
 - Providing technical assistance to labs so they can comply with the Chemical Hygiene Plan, and answer chemical safety questions for employees/students;
 - Working with the laboratory community, administrators and other employees to develop and implement appropriate chemical hygiene policies and practices;
 - Monitoring laboratory chemical inventory and disposal of chemicals used in the laboratories;
 - Developing the University-wide chemical safety inspection and training programs;
 - Assisting Principal Investigators in the selection of appropriate laboratory safety practices and engineering controls for new and existing procedures and projects;
 - Knowing the current legal requirements concerning regulated substances;
 - Investigating all reported accidents that result in the exposure of personnel or the environment to hazardous chemicals;
 - Seeking ways to improve the chemical hygiene program.
 - Assisting Principal Investigators in the selection of appropriate laboratory safety practices and engineering controls for new and existing projects and procedures;
 - Providing the annual review and update of the Chemical Hygiene Plan;
 - Reviewing all reported accident investigations that result in the exposure of personnel or the environment to hazardous chemicals;

- Reviewing and providing technical assistance in decontamination operations where accidents have resulted in significant contamination of laboratory areas;
- Assisting any 24-hour responders or industrial hygienists who are required for emergency operations or quantitative exposure monitoring.

1.3 Definitions

- Laboratory For the purposes of this OSHA standard a "laboratory" is defined as a facility in which hazardous chemicals are handled or manipulated at a "laboratory scale" in reactions, transfers, etc., in small quantities (containers that are easily manipulated by one person) on a non-production (non-manufacturing) basis.
- **Hazardous Chemical** The OSHA Laboratory Standard defines a hazardous chemical as any element, chemical compound, or mixture of elements and/or compounds that is a physical hazard or a health hazard. The standard applies to all hazardous chemicals regardless of the quantity.

A chemical is considered **hazardous** according to the OSHA standard, if it is listed in <u>any</u> of the following:

- OSHA, 29 CFR 1910.1000 Table Z-1 through Z-3;
 - Table Z-1: <u>https://www.osha.gov/laws-</u> regs/regulations/standardnumber/1910/1910.1000TABLEZ1
 - Table Z-2: <u>https://www.osha.gov/laws-</u> regs/regulations/standardnumber/1910/1910.1000TABLEZ2
 - Table Z-3: <u>https://www.osha.gov/laws-</u> regs/regulations/standardnumber/1910/1910.1000TABLEZ3
- The chemical's Safety Data Sheet (SDS)
- Threshold Limit Values (TLV) for Chemical Substances and Physical Agents in the Work Environment, ACGIH (latest edition); or
- The Registry of Toxic Effects of Chemical Substances, NIOSH (latest edition): <u>https://www.cdc.gov/niosh/docs/97-119/</u>
- Physical Hazard Chemical that is classified as posing one of the following hazardous effects: Explosive; flammable (gases, aerosols, liquids, or solids); oxidizer (liquid, solid, or gas); self-reactive; pyrophoric (gas, liquid or solid); self-heating; organic peroxide; corrosive to metal; gas under pressure; in contact with water emits flammable gas; or combustible dust. The criteria for determining whether a chemical is classified as a physical hazard are in <u>Appendix B of the Hazard</u> <u>Communication Standard (§1910.1200)</u> and <u>§1910.1200(c)</u> (definitions of "combustible dust" and "pyrophoric gas").
- Health Hazard A chemical which is classified as posing one of the following hazardous effects: acute toxicity (any route of exposure); skin corrosion or irritation; serious eye damage or eye irritation; respiratory or skin sensitization; germ cell mutagenicity; carcinogenicity; reproductive toxicity; specific target organ toxicity (single or repeated exposure); agents that damage the lungs, skin, eyes or mucus membranes or aspiration hazard. The criteria for determining whether a chemical is classified as a health hazard are detailed in <u>Appendix A of the Hazard Communication</u> <u>Standard (§1910.1200) -- Health Hazard Criteria</u>.

1.4 Hazard Identification for Substances Synthesized in University Laboratories

Some laboratories will synthesize or develop new chemical substances during the course of their research. If the composition of the substance is known and will be used exclusively in the laboratory, the researcher must label the substance and determine, to the best of his/her abilities, the hazardous properties (e.g., corrosive, flammable, reactive, toxic, etc.) of the substance. This can often be done by comparing the structure of the new substance with the structure of similar materials with known hazardous properties. If the chemical produced is of unknown composition, it must be assumed to be hazardous, and appropriate precautions must be taken.

If a chemical substance is produced for another user outside the University, the laboratory producing the substance is required to provide as much information as possible regarding the identity and known hazardous properties of the substance to the receiver of the material. In this case the University has become a manufacturer and the Principal Investigator <u>must</u> generate a Safety Data Sheet (SDS) for the product. Contact EH&S if you have questions or would like assistance in meeting this obligation. Labeling of products that are leaving the University must conform to the requirements of the OSHA Hazard Communication Standard (HCS), 29CFR 1910.1200. More details on the HCS can be found in the University of Rhode Island Hazard Communication Plan. The Hazard Communication plan covers areas of chemical usage that are not covered by the Laboratory Chemical Hygiene Plan. A copy of the Hazard Communication Plan is available at EH&S and may be viewed during normal working hours.

1.5 Chemical Safety Fundamentals

This section outlines the basic compliance and safety elements that lab users need to understand and follow prior to entering the lab.

1.5.1 Chemical Safety Training

All employees and students exposed, or potentially exposed, to hazardous chemicals while performing their laboratory duties must receive information and training regarding the OSHA Laboratory Standard, the URI Chemical Hygiene Plan, and laboratory safety. All laboratory personnel (PIs, staff and students) must attend initial and annual refresher safety trainings provided by EH&S or their college/department. Job-specific training must be provided by departments, principal investigators, laboratory supervisors or other qualified individuals.

EH&S training sessions will describe the:

- Physical and health hazards of various classes of laboratory chemicals;
- Procedures for handling and safely using chemicals present in laboratories;
- How to understand a Safety Data Sheet;
- Appropriate response in the event of a chemical emergency (spill, overexposure, etc.);
- University chemical hygiene policies as codified in this Chemical Hygiene Plan;
- Applicable details of the University's Chemical Hygiene Plan (such as the standard operating procedures for using chemicals); and,
- Hazardous waste management requirements.

All lab training records must be maintained by each PI or lab manager to prove compliance with Federal, State, and University training requirements. Annual initial or refresher training is required for all

laboratory workers and Principal Investigators. Contact EH&S or refer to the EH&S training page for training information.

All current employees/students working with hazardous chemicals who have not attended a chemical safety/hazardous waste training session at the University of Rhode Island must receive this training as soon as possible. New employees must receive training prior to handling potentially hazardous materials. Employees who are transferred to jobs (or are performing tasks) with routine hazards that are different from the hazards of previous jobs or tasks (e.g., exposure to a different class of chemical hazard such as a carcinogen) or new equipment with a specific hazard) must receive additional training from their supervisor or PI outlining the hazards of the new materials, procedures, or equipment prior to starting the new assignment.

When an employee/student is to perform a non-routine task presenting hazards for which he or she has not already been trained, the employee's/student's supervisor will be responsible for discussing with the employee the hazards of the task and any special measures (e.g., personal protective equipment or engineering controls) that must be used to protect the employee/student. Additional laboratory-specific safety training must be provided by your laboratory supervisor or Principal Investigator when new hazardous chemicals are introduced into the laboratory. EH&S is available to consult with the supervisor or employee/student, as necessary.

Every laboratory worker must know the location and proper use of available protective clothing and equipment, emergency equipment, as well as emergency procedures. Information on protective clothing and equipment is contained in Chapter 2 of this plan.

1.5.2 Container Labeling

All new containers of hazardous chemicals that pose a physical or health hazard to an exposed lab worker must have a label attached per OSHA's Hazard Communication standard. Labels on manufactured hazardous chemicals must include:

- Product Identifier (Chemical Name, CAS #, Code)
- Pictogram(s)
- Signal Words: (Danger or Warning) "Danger" is used for the more severe hazards, and "Warning" for the less severe hazards.
- Hazard Statement: Standard phases to describe the hazard class (Physical, Health or Environmental).
- Precautionary Statement: A phrase to describe measures to be taken to prevent adverse effects, PPE and first aid included.
- Supplier/Manufacturer Information: address and phone numbers.

Labels on new containers from the manufacturer or vendor will provide you with additional safety information to help you protect yourself while working with this substance. This includes protective measures to be used when handling the material, clothing that should be worn, first aid instructions, storage information and procedures to follow in the event of a fire, leak, or spill.

If you find a container with no label, report it to your supervisor. You should also report labels that are torn or illegible so that the label can be replaced immediately. **Existing labels on new containers of hazardous chemicals should never be removed or defaced, except when the container is empty**. If you use secondary working containers (OSHA defines these as "portable" containers) that will take more than one eight-hour work shift to empty, or if there is a chance that someone else will handle the container before you finish using it, you must label it with the chemical name and hazard. This is part of your responsibility to help protect other lab users. The label and information must be in English, without abbreviations, and contain the following information (at a minimum):

- Product Identifier (Chemical Name, CAS #, Code)
- Pictogram(s)
- Signal Words: (Danger or Warning) "Danger" is used for the more severe hazards, and "Warning" for the less severe hazards.
- Hazard Statement: Standard phases to describe the hazard class (Physical, Health or Environmental).

Contact the chemical manufacturer or vendor if new containers of product do not have proper labels.

1.5.3 Safety Data Sheets (SDS)

A Safety Data Sheet, often referred to by its acronym "SDS", is a detailed informational document prepared by the manufacturer or importer of a hazardous chemical to describe the physical and chemical properties of the product. Information included in an SDS helps employers and employees understand the potential health and physical hazards of the chemical, aids in the selection of proper Personal Protective Equipment (PPE), and describes how to respond effectively to exposure situations. It should be noted that the health and safety guidance in the SDS often addresses the worst-case situation which would be more relevant to a major industrial accident or tank car spill than to a laboratory. The SDS is not always helpful in selecting appropriate safeguards in the laboratory. If you have questions about handling or protecting yourself from a particular chemical contact your supervisor or EH&S.

Each Principal Investigator/laboratory supervisor is responsible for obtaining the SDSs for the chemicals used in his/her laboratory. SDSs can be obtained from the manufacturers, chemical distributors, or from URI's online SDS vendor: Chemwatch. Chemwatch can be accessed directly from URI's Environmental Health and Safety home page <u>https://web.uri.edu/EH&S/</u>. Manufacturers/vendors are required to provide an SDS with the first shipment of a product. Please contact EH&S if you have any questions about obtaining an SDS for a particular chemical via Chemwatch or the manufacturer.

The standard format of an SDS contains 16 sections. These sections are described below:

Section 1, Identification includes product identifier; manufacturer or distributor name, address, phone number; emergency phone number; recommended use; restrictions on use.

Section 2, Hazard(s) identification includes all hazards regarding the chemical; required label elements.

Section 3, Composition/information on ingredients includes information on chemical ingredients; trade secret claims.

Section 4, First-aid measures includes important symptoms/effects, acute, delayed; required treatment.

Section 5, Fire-fighting measures lists suitable extinguishing techniques, equipment; chemical hazards from fire.

Section 6, Accidental release measures lists emergency procedures; protective equipment; proper methods of containment and cleanup.

Section 7, Handling and storage lists precautions for safe handling and storage, including incompatibilities.

Section 8, Exposure controls/personal protection lists OSHA's Permissible Exposure Limits (PELs); ACGIH Threshold Limit Values (TLVs); and any other exposure limit used or recommended by the chemical manufacturer, importer, or employer preparing the SDS where available as well as appropriate engineering controls; personal protective equipment (PPE).

Section 9, Physical and chemical properties lists the chemical's characteristics.

Section 10, Stability and reactivity lists chemical stability and possibility of hazardous reactions.

Section 11, Toxicological information includes routes of exposure; related symptoms, acute and chronic effects; numerical measures of toxicity.

Section 12, Ecological information

Section 13, Disposal considerations

Section 14, Transport information

Section 15, Regulatory information

Section 16, Other information, includes the date of initial preparation or last revision.

1.5.4 Signs

Prominent signs of the following types <u>must</u> be posted in each laboratory:

- The University of Rhode Island Hazard Communication Sign. See the EH&S web page: <u>https://web.uri.edu/EH&S/chemical/</u> for a fillable sign that can be printed out. This sign shall be posted on the outside door of each laboratory so lab users, visitors and emergency responders may know the chemical, biological, radioactive and other hazards without entering the room. If possible, place the sign inside a protective plastic cover. Update the sign as needed as personnel and hazards change. The sign shall include the telephone numbers of emergency personnel/facilities, supervisors, and laboratory workers, and the various types of hazards present in an individual room. The sign must contain a 24/7 phone number (not an office phone number) of the PI or other lab manager in case of an emergency;
- Signs identifying locations for safety showers, eyewash stations, portable fire extinguishers, other safety and first aid equipment, and exits;
- Signs identifying the location of the satellite accumulation area(s) (SAA). Refer to the EH&S web page: <u>https://web.uri.edu/EH&S/hazardous_waste/</u> to print a copy or contact EH&S;
- Signs identifying areas where certain hazardous chemicals or equipment are used or stored, if applicable. This would include the use of latex gloves, chemotherapy or other hazardous drugs, carcinogens, lasers or x-ray equipment, etc. Refer to Section 2.2 for additional information.

1.6 Chemical Exposure Assessment

Routine environmental or employee exposure monitoring of airborne concentrations is not usually warranted or practical in laboratories because chemicals are typically used for relatively short time periods, in small quantities, and within a vented device (fume hood, BSC or glove box). However, sampling may be appropriate when a highly toxic substance is used regularly (3 or more separate handling sessions

per week), is used for an extended period of time outside of ventilation equipment (greater than 1 to 2 hours at a time) or is used in especially large quantities.

EH&S personnel must be notified by the PI or lab users when this occurs, and EH&S will recommend follow-up exposure assessments as necessary. EH&S personnel will ask questions to qualitatively estimate employee exposures to laboratory chemicals. The exposures to laboratory employees who suspect and report that they have been over-exposed to a toxic chemical in the laboratory, or are displaying symptoms of over-exposure to toxic chemicals, will also be assessed. This assessment will initially be qualitative and, based upon the professional judgment of the investigating safety professional, may be followed up by specific quantitative monitoring. A memo, or report, documenting the quantitative assessment will be sent to the employees involved and their supervisors, as well as, to the URI Human Resource Administration in the case of a reported over-exposure.

Individual concerns about excessive exposures occurring in the laboratory should be brought to the immediate attention of EH&S and your supervisor. Any person who believes they have received an over-exposure to a hazardous chemical should file an accident/incident report, form USP14A, with the URI Human Resource Administration at the time of the event.

1.7 Medical Consultation and Examination

The University of Rhode Island will provide employees and lab users who work with hazardous chemicals an opportunity to receive medical consultation, including any follow-up examinations which the examining physician or occupational health professional determines to be necessary, under the following circumstances:

- Where exposure monitoring indicates air concentration levels over the action level for an OSHA regulated substance that has medical surveillance requirements;
- Whenever a laboratory employee develops signs or symptoms that may be associated with a hazardous chemical to which the employee may have been exposed in the laboratory;
- Whenever a spill, leak, or explosion results in the likelihood of a hazardous exposure, as determined by the Chemical Hygiene Officer.

All examinations shall be provided by a physician licensed in Occupational Medicine or under the direct supervision of a physician licensed in Occupational Medicine, at no cost to the employee, without loss of pay, and at a reasonable time and place. Students may seek medical attention from a Certified Occupational Health Nurse Specialist at URI Health Services.

When medical consultations or examinations are provided, the examining physician shall be provided with the following information:

- The identity of the hazardous chemical(s) or material(s) to which the employee may have been exposed and the SDS, if available;
- A description of the conditions under which the exposure occurred including quantitative exposure data, if available, and;
- A description of the signs and symptoms of exposure that the employee is experiencing, if any.

For examinations or consultations provided to employees, a written opinion from the examining physician shall be obtained by the URI Human Resource Administration. It shall include:

• Recommendations for further medical follow-up;

- Results of the examination and associated tests;
- Any medical conditions revealed that places the employee at an increased risk of exposure to a hazardous substance found in the workplace; and
- A statement that the employee has been informed of the results of the examination or consultation.

EMERGENCIES: Individuals with life threatening emergencies should proceed immediately to the hospital emergency room. An ambulance can be obtained by dialing 911. A copy of the Safety Data Sheet should accompany the patient to the hospital. Employees must file an accident report <u>https://web.uri.edu/hr/fileswork-related-incidentinjury-procedure/</u>, form USP14A, with the URI Human Resource Administration, detailing what event occurred, what the chemical substance was that caused the symptoms and a description of the over-exposure. Students should file accident reports at health services at the Potter Building. If the employee/student is unable to file the report due to his/her injuries the report should be filed by the Laboratory Supervisor and signed by the Department Chair.

1.8 Laboratory Safety Inspection Programs

EH&S conducts inspections of all University laboratories handling or storing hazardous chemicals. These inspections evaluate the following:

- Potential employee exposures (qualitative assessments);
- The status of critical engineering control equipment (hoods and safety showers);
- The handling and storage of chemicals;
- The use of personal protective equipment;
- Hazardous waste management (labeling and containment);
- Employee training; and
- Compliance with Federal/State regulations and University policies.

Each University laboratory is inspected on a regular basis (at least annually) by EH&S staff. Laboratory inspections are completed using a web-based inspection program. Pls/laboratory supervisors should contact EH&S to obtain login information and training on this inspection program. Following the inspection, Pls will be notified via email if any issues were documented in their lab and how to correct them. All deficiencies must be corrected by logging into the inspection module and closing each issue out within the time period designated by EH&S. Principal Investigators/laboratory supervisors must conduct more frequent inspections to make sure that needed safety equipment and personal protective equipment (PPE) is in place and functional, the hoods are working, the hazardous waste accumulation area is maintained per EPA/RIDEM requirements, and that the lab is maintained in a neat and orderly condition. A copy a self-inspection Laboratory Inspection Report Form can be found at the following link: https://web.uri.edu/ehs/chemical/.

1.9 Prior Approval

Under some circumstances a particular chemical may be considered sufficiently hazardous as to require prior approval from EH&S before research begins.

1.10 Standard Operating Procedures (SOPs)

A list of chemicals requiring an SOP can be found in Section 2.2. The PI may also establish which hazardous chemicals, equipment and/or procedures require an SOP in his/her laboratory. He/she will develop

laboratory and chemical-specific written Standard Operating Procedures (SOPs) to document these hazardous operations and use of hazardous chemicals. Refer to Section 2.2 of this document for additional information in preparing an SOP.

1.11 Respiratory Protection Program for Laboratories

The University minimizes employee respiratory exposure to potentially hazardous chemical substances through engineering methods (such as local exhaust ventilation and hoods) and through the implementation of administrative controls (written standard operating procedures (SOPs), use of safe work practices, training etc.). It is recognized, however, that for certain situations or operations, the use of these controls may not be feasible or practical. Under these circumstances, or while such controls are being instituted, or in emergency situations, the use of personal respiratory protective equipment may be necessary.

Any Department/Principal Investigator needing to use respirators must contact EH&S prior to use so the user may be considered for inclusion in the Respiratory Protection Program. This program includes the following respirator program components: exposure assessment; respirator selection; medical approval and surveillance; fit testing; user training; inspection/repair; cleaning/disinfection; and storage. Each of these program components is required by OSHA's respiratory protection standard (29 CFR 1910.134) in all situations where respirators are used. If you are using a respirator and are not included in the University's respiratory protection program, contact your supervisor and EH&S. Principal Investigators are responsible for providing respiratory protective equipment if such equipment is required.

1.12 Medical Record Keeping

All exposure assessments and occupational medical consultation/examination reports will be maintained in a secure area in the employee's personnel file in accordance with OSHA's medical records rule (29CFR 1910.1020) by URI Human Resources. Individuals may obtain copies or read their report by making a request in writing to URI Human Resources. Records will be retained for 30 years after the termination date of the employee.

1.13 Laboratory Decommissioning

It is the responsibility of the Principal Investigator and Department Chair to assure that all laboratories are properly decommissioned whenever a laboratory is vacated, renovated, or relocated. All chemicals, biohazards, and radioactive materials must be properly relocated, reallocated or disposed before the PI leaves campus. The laboratory must be decontaminated from all chemical, biological, or radioactive hazards. **Each PI must be familiar with URI's** *Laboratory Cleanout Policy* and *Cleanout Procedures* which includes completing a Laboratory Clearance Form. Refer to EH&S's home page for links to this form. EH&S must be contacted <u>at least four weeks</u> prior to their departure in order to assist with the clearance process.

1.14 Hazmat Security

Access to University premises, identified as high hazard areas, shall be limited to authorized University staff and students or other persons on official University-related business. Measures must be taken to assure that persons entering these areas are appropriately trained, adequately protected from hazards, and informed about the safety and emergency procedures relevant to their activities.

A high hazard area is defined as any area where any of the following activities or items is present:

- Hazardous chemicals: carcinogens, reproductive hazards, highly toxic, corrosive, etc.
- Biohazards (infectious agents)
- Radioactive materials
- Physical hazards: cutting hazards, falling hazards, hydraulic equipment, etc.

Laboratory security is an integral part of an effective safety program. Follow these procedures to ensure a secure working environment in your laboratory.

- Keep laboratory locked when unattended.
- Keep all hazardous chemicals, drug precursors, controlled substances, radioactive materials, and biohazards in secure, locked locations.
- Keep accurate records and inventories of chemicals, stocks, cultures, project materials, growth media, and other related laboratory items.
- Notify Campus Police at 911 if any laboratory items are missing.
- Inspect all packages arriving at the work area. Make sure all packages are properly labeled and undamaged before accepting deliveries.
- When research is completed for the day, ensure that all chemicals, biohazards, and radioactive materials are properly stored and secured.
- Ask strangers to leave the room if they are not authorized to be there.
- Contact Campus Police at 911 if you observe suspicious behavior.

1.15 Shipping Hazardous Materials/Dangerous Goods

All packages offered for shipment containing hazardous materials under the Department of Transportation (DOT) regulations or as Dangerous Goods (DG) as defined by the International Air Transport Association (IATA) through a common carrier such as the U.S. Postal Service, Federal Express (FedEx), United Parcel Service (UPS), or other commercial carrier must be packaged, marked, labeled, and documented properly. Dangerous goods are substances or materials that are capable of posing a risk to health, safety, or property. This can include hazardous substances, hazardous waste, marine pollutants and elevated temperature materials. Also included are laboratory chemicals, radioactive materials, lithium batteries, dry ice, compressed gases, biological agents, diagnostic specimens, refrigerants and instruments or equipment that might contain hazardous materials. Materials that are shipped to labs for testing or analysis, to a colleague for collaborative research, to another research facility, returned to the manufacturer or sent to a field research site must all follow applicable shipping requirements.

Staff and students are <u>prohibited</u> from shipping hazardous materials without proper training. Failure to comply with the hazmat shipping requirements may result in large criminal and civil fines and penalties. EHS personnel have received special training in shipping hazardous materials. Call EH&S for information and assistance in shipping hazardous materials or to inquire as to whether your material falls under these regulations. Training for some shipping, such as dry ice, is available through CITI. Contact EHS for registration information.

Chapter 2.0 Standard Operating Procedures for Laboratory Chemicals

2.1 General Guidelines

The **engineering** and administrative controls that must always be considered first when reducing or eliminating exposures to hazardous chemical include:

Substitution of a less hazardous substance;

Scaling down the size of experiment;

Substitution of less hazardous equipment or process (e.g., safety cans for glass bottles);

Isolation of the operator or the process;

Local and general ventilation (e.g., use of fume hoods).

2.1.1 Generic Standard Operating Procedures for Handling Laboratory Chemicals

The procedures listed below are the generic Standard Operating Procedures (SOPs) for all URI laboratories.

- <u>Plan ahead</u>. Seek information about the hazards, plan protective procedures to minimize exposure to chemicals, and plan the safe positioning of laboratory apparatus before beginning any new operation.
- <u>Carefully read the label and SDS **before** using a chemical</u>. The manufacturer's or supplier's Safety Data Sheet (SDS) will provide special handling information. In lieu of the paper copy of the manufacturer's SDS, you can also access Chemwatch, an on-line database of SDSs. A link to Chemwatch can be found on EH&S's web page.
- <u>Be aware of the hazards existing in the laboratory and the appropriate safety precautions</u>. Know the location and proper use of emergency equipment, the appropriate procedures for responding to emergencies, and the proper methods for storage, transport and disposal of chemicals within the facility.
- Do not work alone in the laboratory while conducting hazardous operations or working with hazardous chemicals. If you must work alone or in the evening in a laboratory containing hazardous materials, you must have prior approval from the Principal Investigator/Laboratory Supervisor. Let someone else know and have him/her periodically check on you.
- <u>Students and employees should have prior approval for hazardous operations from the Principal</u> <u>Investigator/Laboratory Supervisor</u>.
- <u>Label all non-original chemical containers with appropriate identification and hazard information</u>. (See Section 1.5.2, *Container Labeling*).
- Use only those chemicals for which you have the appropriate exposure controls (such as a chemical fume hood) and administrative programs/procedures (training, restricted access, etc.) in place.
- <u>Always use adequate ventilation with chemicals</u>. Operations using volatile substances having workplace standards (Permissible Exposure Limits) at or below 50 ppm must be performed in a chemical fume hood. If you are unsure of the Permissible Exposure Limits, use a fume hood as a precaution or contact EH&S for assistance.
- Use hazardous chemicals and all laboratory equipment only for their intended purposes.
- <u>Inspect equipment or apparatus for damage before adding a hazardous chemical</u>. Do not use damaged equipment.
- <u>Inspect personal protective apparel and equipment for integrity or proper functioning before each</u> <u>use</u>.
- Under no circumstances should a fume hood or BSC be used that is not functioning properly or uncertified. <u>Malfunctioning laboratory equipment such as hoods should be labeled or tagged "out of</u>

service" so that others will not inadvertently use it before repairs are made. Contact Facilities Services at 874-4060 for hood repairs. Contact the Biosafety Officer for BSC repairs at 874-7993.

- <u>Do not dispense more of a hazardous chemical than is needed for immediate use</u>. Keep chemicals that are not being used stored in cabinets or shelves rather than on the lab bench.
- <u>Visitors to the laboratory must use proper PPE (safety glasses) and are to be escorted by an authorized employee or student and are the responsibility of that employee or student</u>. Only authorized persons are allowed in University laboratories.
- Experiments that may need to run continuously or overnight need special planning to prevent the release of hazardous substances in the event of interruptions of utility services, (no electricity, cooling water, etc.). Fume hoods will not work when the electricity is off. Post signs with the telephone number of the responsible person, leave the lights on, and try to make periodic inspections. All unattended operations must have prior approval from the Principal Investigator/laboratory supervisor.
- <u>Plan for pollution prevention in every step of the experiment</u>. Purchase, use, and store the minimum amount of all hazardous materials. Chemicals should not be purchase in amounts that cannot be used up within one year.
- <u>Responsibility for chemicals and chemical waste generated within the lab rests with the Principal</u> <u>Investigator</u>.
- <u>All hazardous waste disposal must be in compliance with EPA and RIDEM regulations</u>. Contact EH&S for assistance.
- <u>Be alert to unsafe conditions and correct any that you detect</u>. Contact EH&S for assistance.

2.1.2 Personal Hygiene

The restrictions below shall be followed for all URI laboratories:

- Never smell, inhale or taste any chemical.
- Do not touch doorknobs, light switches, phones, etc., while wearing (contaminated) gloves. Disposable gloves should be removed by turning them inside out to prevent contaminating yourself; when done correctly, the contaminated surface will end up as the inside of the glove. Ask the Chemical Hygiene Officer to demonstrate the proper technique if you are uncertain of the correct procedures or refer to the CDC poster provided <u>here</u>. Reusable gloves should be cleaned between uses. Disposable gloves are not to be re-used.
- Avoid direct contact with any chemical. Keep chemicals off your hands, skin, face, and clothing, including shoes. If clothing becomes contaminated, remove it and gloves and wash your hands thoroughly with soap and water before leaving the laboratory. Send grossly contaminated clothing to Pier Cleaners or the approved URI dry cleaner vendor. Do not launder it at home. Do not store backpacks and personal items near hazardous chemicals as they may become contaminated and there is a risk of taking the contamination home with you.
- Smoking, drinking, eating, and the application of cosmetics are prohibited in laboratories where hazardous chemicals are used. Food and beverage containers are barred from the laboratory.
- Never pipette hazardous materials, chemicals, radionuclides, or biohazards by mouth. Use a pipette bulb or other mechanical pipetting device.
- Do not store or consume food or drink in the laboratory. Refrigerators and microwaves are exclusively for lab use. Mark all such refrigerators and microwaves "Not for Food". Mark all food or beverage products that are utilized in laboratory experiments as "Not for Human Consumption".

2.1.3 Housekeeping

The following safety precautions shall be followed for all University of Rhode Island laboratories:

- All laboratory areas must be maintained in a clean and safe condition.
- Keep floors clean and dry. Keep all aisles, hallways, and stairs clear of all chemicals. Stairways and hallways should not be used as storage areas.
- Keep all work areas, and especially work benches, clear of clutter and obstructions. Clutter presents opportunities for accidents.
- All work surfaces should be cleaned regularly.
- Access to emergency equipment, utility controls, showers, eyewashes and exits should never be blocked. Do not store supplies or equipment in or around the eyewash and safety shower areas.
- Hazardous wastes should be kept in the appropriate containers in the Satellite Accumulation Area (SAA) and labeled properly. Caps should be tightly sealed.
- All containers must be properly labeled. This includes in-use materials, stored chemicals, biohazards, radioactive materials, and hazardous wastes.
- Sharps such as razor blades, scalpels, syringes, Pasteur pipets (1 ml or less), needles, or biologically contaminated broken glass must be placed in impervious, puncture resistant containers, made of rigid plastic or metal. The container must be a labeled "Sharps" container. If the sharps are contaminated with biohazardous material, then the international "biohazard" symbol label must also be affixed to the container. If razor blades are used it is recommended that these blades be pushed into a Styrofoam block when not in use to prevent accidental cuts.
- Broken glassware should be placed in a specially marked laboratory glassware container or a cardboard box lined with a plastic bag to contain glass chips. When full, lab staff are responsible for sealing the box, labelling the outside "Broken Glass" and disposing the box to the dumpster. Do not discard laboratory in the blue recycling bins that are used for beverage containers. Consult with EH&S if the glassware is severely contaminated with hazardous chemicals. Sharps are disposed as biomedical waste. Contact EH&S for additional instructions for biomedical waste.

2.1.4 Glassware Safety

- Handle and store laboratory glassware with care. Do not use damaged glassware. Borosilicate
 glassware is recommended for all laboratory glassware except for special experiments that use UV or
 other light sources. Borosilicate glassware can be used at very high temperatures. Lab glass cannot be
 recycled because the temperature used for recycling glass is too low to melt borosilicate glass.
- Any glass equipment to be evacuated, such as suction flasks, should be specially designed with heavy walls. To protect users and other laboratory occupants, wrap older setups without heavy walls with netting or other material to contain flying shards in the event of a rupture. Glass vessels even at reduced pressure can collapse violently, either spontaneously (if cracked or weakened) or from an accidental blow. Use extra care with Dewar flasks and other evacuated glass apparatus; shield or wrap them with cloth-backed friction or duct tape to contain chemicals or fragments should implosion occur.
- Work with pressurized glass/plastic vessels or evacuated vessels requires the use of the following personal protective equipment (PPE): face shield, safety goggles or glasses depending on the substance in the vessel, long-sleeved lab coat, and closed toe, non-perforated shoes.

2.2 Laboratory-Specific Written Standard Operating Procedures Required

It is the responsibility of Principal Investigators to write Laboratory-Specific Standard Operating Procedures (SOPs) to cover the use of hazardous chemicals, hazardous drugs, reproductive toxins

(including chemotherapy drugs), and carcinogens, as well as, processes or equipment that may be hazardous. The SOP must be reviewed and approved by EH&S. Upon approval, the PI must review the SOP with all lab users and have each lab user sign off that they understand the specific procedures and hazards contained in the SOP.

The following is a list of chemicals that require a laboratory specific SOP:

Chemical	Chemical Lists and Reference
Antineoplastic (Chemotherapy) and Other	https://www.cdc.gov/niosh/docs/2016-161/pdfs/2016-
Hazardous Drugs	161.pdf?id=10.26616/NIOSHPUB2016161
Antineoplastic (Chemotherapy) and Other	https://www.cdc.gov/niosh/docs/2016-161/default.html
Hazardous Drugs under consideration or	
recently included in the list of hazardous	
drugs by the CDC	
Carcinogens or suspected carcinogens	https://www.cdc.gov/niosh/topics/cancer/npotocca.html#a
	https://www.osha.gov/SLTC/carcinogens/standards.html
Dimethyl mercury	https://www.osha.gov/dts/hib/hib_data/hib19980309.html
Compressed gasses with NFPA rating 3 & 4 or	See Appendix I
pyrophoric	

Note that this is a partial list of chemicals that require a SOP. PIs shall create an SOP for other hazardous chemicals (i.e. explosive salts, acutely toxic chemicals, peroxide forming chemicals, strong corrosives, strong oxidizing agents, strong reducing agents, water reactive chemicals), as well as biological agents (i.e. tetrodotoxin), radiological material and dangerous processes and equipment. SOPs must be submitted to EH&S for review prior to using these chemicals, biological agents, radiological material, dangerous equipment and processes. EH&S may require up to four weeks to review a SOP. Contact EH&S for additional information or guidance as to whether an SOP is necessary for a specific chemical, equipment or procedure.

A template SOP form is provided on the EH&S web page. Copies of the SOPs (including the student sign off page) will be maintained on file and reviewed with lab users on a regular basis. OSHA requires proper signage for certain carcinogens. Proper signage for OSHA listed carcinogens (see OSHA link in table above) must have identical verbiage (but not necessarily design) to the signage provided below:



The top sign shall be placed in the entrance to laboratories where carcinogens are in use. The second (lower) sign shall be placed during cleanup of large spills, maintenance, or repair operations on contaminated systems or equipment, or any operations involving work in an area where direct contact with a carcinogen.

2.2.1 When to Review an Existing Standard Operating Procedure

Laboratory workers should not proceed with familiar tasks until the safety aspects are reviewed and shared with all other laboratory workers. Hazards may exist that are not fully recognized.

Lab workers should review SOPs periodically to identify any previously unrecognized hazards. Once identified, the SOP should be updated to reflect any change made to improve overall safety. It may be helpful to review SOPs from institutions with strong science and engineering programs.

Specific indicators (procedural changes) that should cause the lab worker to stop and review the safety practices of their procedure include:

- A new procedure, process, or test is introduced, even if it is very similar to older practices.
- A change or substitution of any of the ingredient chemicals is made in a procedure.
- A substantial change is made in the amount of chemicals used (scale-up of experimental procedures); one should review safety practices if the volume of chemicals used increases by 20% or more.
- A failure of any part of the equipment used in the process has occurred, especially safeguards such as chemical fume hoods.
- Unexpected experimental results (such as a pressure increase, increased reaction rates, unanticipated byproducts) have occurred. When an experimental result is different from the predicted, a review of how the new result may affect safety practices should be made.
- Chemical odors or illness in the laboratory staff that may be related to chemical exposure, or other indicators of a failure in engineered safeguards (hoods, glove boxes, etc.) is observed.

The occurrence of any of these conditions should immediately cause the researcher to pause, evaluate the safety implications of these changes or results, make changes to the written laboratory-specific Standard Operating Procedures as necessary, and proceed cautiously. If they have been designated to change or update the Standard Operating Procedures, laboratory workers and students must obtain final approval from the Principal investigator/laboratory supervisor before making any changes. Contact EH&S for assistance in reviewing laboratory conditions when needed.

2.3 Protective Clothing and Laboratory Safety Equipment

2.3.1 General Considerations - Personal Protective Clothing/Equipment (PPE)

Personal protective clothing and equipment should be selected only after carefully conducting a Risk Assessment. PPE should be used in conjunction with engineering and administrative controls; it is not a substitute for either. PPE only puts a protective barrier between the lab worker, while Engineering Controls remove the hazard and Administrative Controls allow the lab worker to manage the hazard and work safely with it. The Safety Data Sheet (SDS) will list the personal protective equipment (PPE) recommended for use with the chemical. Note that the SDS addresses worst-case conditions for manufacturers where large quantities are in use., Thus, all the equipment listed may not be necessary for a specific laboratory scale task. However, the following personal protective equipment should be used at the University of Rhode Island whenever handling extremely hazardous chemicals: long-sleeved lab coat

(or flame-resistant lab coat if working with pyrophorics), gloves, protective eyewear, and sturdy, closed toe shoes.

OSHA Personal Protective Equipment Standards [29CFR 1910.132-138] for eye, face, head, foot, and hand protection mandate a hazard assessment at each workplace. The Principal Investigator is responsible for conducting the hazard assessment in each of his/her laboratories. If hazards are determined to be present, it is required that the proper PPE be selected, provided by the Principal Investigator or department, and used by each affected staff and lab user. Training is mandatory for all staff and lab users that are assigned PPE. Both the hazard assessment and employee training require written certification. The template SOP form (see EH&S web page) provides a place for documenting that training on the SOPs has occurred. When laboratory procedures and personnel change, these SOP's must be updated. Your supervisor, other sections of this plan, or EH&S can assist you in determining which personal protective devices are required for each task. Remember that there is no harm in being overprotected. Departments/principal investigators must provide appropriate personal protective equipment to employees at no charge to the employee.

2.3.2 Protection of Skin and Body

Skin and body protection involve wearing protective clothing over all parts of the body that could become contaminated with hazardous chemicals. Personal protective equipment (PPE) should be selected on a task basis and checked to ensure it is in good condition prior to each use (e.g., no pinholes in gloves). Even where there is no immediate danger to the skin from contact with a hazardous chemical it is still prudent to wear clothing that minimizes exposed skin surfaces when working in chemical laboratories. Employees should wear long-sleeved/long-legged clothing and avoid tank tops, shorts, leggings, or very short skirts. A laboratory coat should be worn over street clothes and be laundered regularly at a commercial laundromat (contact your PI or lab supervisor for vendor information) when handling hazardous chemicals, biohazards or radioactive materials. Laboratory coats are intended to prevent contact with dirt, chemical dusts and minor chemical splashes or spills. If the lab coat becomes contaminated it should be worn in the laboratory at all times. Sandals are not allowed in laboratories. In addition, long hair, dangling jewelry, and loose clothing should be confined or removed as these items may become entangled in apparatus or dangle in chemical containers. Some non-natural clothing fabrics such as rayon burn very readily (and adhere to the skin) and are not recommended for use in a chemical laboratory.

Additional protective clothing may be required for some types of procedures or with specific substances such as when carcinogens or large quantities of corrosives, oxidizing agents or organic solvents are handled. This clothing may include impermeable chemically resistant aprons and gloves, as well as, plastic-coated coveralls, shoe covers, and arm sleeves. Protective sleeves should always be considered when wearing an apron. These garments can either be washable or disposable in nature. They should never be worn outside the laboratory. The choice of garment depends on the degree of protection required and the areas of the body which may become contaminated. Rubberized aprons, plastic coated coveralls, shoe covers, and arm sleeves offer much greater resistance to permeation by chemicals than laboratory coats and, therefore, provide additional time to react (remove the garment and wash affected area) if contaminated.

If you are working with substances of high acute or chronic toxicity and wearing washable garments (such as a laboratory coat), contact your PI or laboratory supervisor about the URI approved vendor to launder these items. These items should not be laundered at home due to the potential for cross contamination with clean clothes and exposure to others. Wear disposable garments if available and approved by the PI.

For work where contamination is possible, special attention must be given to sealing all openings in the clothing. Tape can be utilized for this purpose. In these instances, caps should be worn to protect hair and scalp from contamination.

Chemical resistant gloves should be worn whenever the potential exists for contact with corrosive or toxic substances and substances of unknown toxicity. In some cases, it may be prudent to "double glove", that is, wear two pair of gloves simultaneously. Gloves should be selected on the basis of the materials being handled, the particular hazard involved, and their suitability for the operation being conducted. Common glove types include butyl rubber, neoprene, PVC (vinyl), nitrile, latex and teflon (Silvershield)[®]. Before each use, gloves should be checked for integrity. Gloves should be washed prior to removal whenever possible to prevent skin contamination. Non-disposable gloves should be replaced periodically, depending on frequency of use and their resistance to the substances handled.

Protective garments are not equally effective for every hazardous chemical. Some chemicals will "break through" the garment in a very short time. The glove thickness, chemical resistance, chemical permeability, and break-through time are some important parameters to consider when selecting the appropriate glove. Therefore, garment and glove selections are based on the specific chemical utilized. Contact EH&S for personal protection equipment selection assistance or information. Glove manufacturers' web sites and other web sites such as NIOSH can provide excellent glove selection guides.

Latex Allergies: Many individuals who have used latex products such as latex gloves have developed severe allergies to latex. There are three categories of latex allergies:

- 1. Contact dermatitis,
- 2. Allergic contact dermatitis (delayed hypersensitivity), and
- 3. Immediate hypersensitivity latex allergy.

Reaction to latex may manifest through skin rashes, hives, itching, swollen skin, swollen lips and tongue, shortness of breath, fainting, eyes or sinus symptoms, asthma and difficulty breathing, coughing spells, wheezing, and shock. The use of latex gloves is not recommended for use with hazardous chemicals if there is an alternate available that provides the needed degree of chemical protection or if there is a latex-sensitive individual working in the laboratory.

EH&S requires that this sign also be posted in all University laboratories where latex gloves are in use to warn individuals who may have a latex allergy. Post the sign on the door of the lab as well as in the areas where the latex gloves are stored and used. The letter size must be at least three eighths (3/8) of an inch high. The following is an example of a typical sign for the use of latex gloves.



2.3.3 Eye Protection

Eye protection is required for all personnel, students, and any visitors present in locations where chemicals are handled, or where there is a possibility of eye impact injuries from failure of pressurized vessels, glassware that may shatter on impact or equipment that has rotating shafts). The selection of appropriate safety glasses, goggles, or goggles with a face shield, to be worn in the laboratory must be based upon the physical state, the type of operation, and the level of hazard of the chemical used. Safety glasses effectively protect the eye from solid materials (dusts and flying objects) but are less effective at protecting the eyes from chemical splash to the face. Goggles should be worn in situations where chemicals or hot (>60 degrees Celsius) liquids are handled and chemical splashes to the face are possible. Goggles form a liquid-proof seal around the eyes, protecting them from a splash. When handling highly reactive substances or large quantities of hazardous chemicals, including corrosives, poisons, and hot chemicals, goggles with a face shield should be worn. It is the Principal Investigator's responsibility to assure that properly -fitting, appropriate eye protection is available to all lab users, including visitors if they are allowed in the laboratory.

Contact lenses can increase the risk of eye injury if worn in the laboratory - particularly if they are of the gas-permeable variety. Gases and vapors can be concentrated under these lenses and cause permanent eye damage. Chemical splashes to the eye can get behind all types of contact lenses. Once behind a lens the chemical is difficult to remove with a typical eyewash. For these reasons it is recommended that prescription glasses (not contact lenses) be worn in laboratories. If they are worn, the use of chemical splash goggles is recommended. Some safety glasses and goggles can accommodate prescription glasses and should be used when possible. The use of lasers or welding requires special protective eyewear. Consult with EH&S if you need help with choosing the correct eye protection.

2.3.4 Protection of the Respiratory System

Inhalation hazards can be controlled using ventilation or respiratory protection. Check the label and SDS for information on a substance's inhalation hazard and special ventilation requirements. When a potential inhalation hazard exists a substance's label or SDS contains warnings such as:

"Use with adequate ventilation" "Avoid inhalation of vapors" "Use in a fume hood" "Provide local ventilation" Take appropriate precautions before using these substances. Controlling inhalation exposures via engineering controls (ventilation or hoods) is always the preferred method. As with other personal protective equipment, respiratory protection relies heavily on employee work practices and training to be effective.

2.3.4.1 Use of Respirators

Respirators are designed to protect against specific types of substances in limited concentration ranges. Respirators must be selected based on the specific type of hazard (toxic chemical, oxygen deficiency, etc.), the contaminant's anticipated airborne concentration, and required protection factors.

Types of respiratory protective equipment include:

- Particle-removing air purifying respirators
- Gas and vapor-removing air purifying respirators
- Atmosphere supplying respirators

Respirators are not to be used except in conjunction with a complete <u>respiratory protection program</u> as required by OSHA (see <u>29 CFR 1910.134</u>). If your work requires the use of a respirator, contact your Principal Investigator/laboratory supervisor and EH&S. EH&S and URI Health Services can assist you in meeting all elements of the written respiratory protection plan. Users of respirators must be thoroughly trained in proper use, maintenance, storage and limitations of this equipment, the nature of the respiratory hazard, and the signals of respirator failure (odor breakthrough, filter clogging, etc.).

2.3.5 Laboratory Safety Equipment

2.3.5.1 Chemical Fume Hoods

Laboratory air should be continuously replaced. An exchange rate of 6 to 10 air changes per hour is normally adequate general ventilation if local exhaust systems such as hoods are used as the primary method of chemical exposure control. Air flow should be directed from non-laboratory areas into laboratories and then exhausted out of the building. Leave the hood on when it is not in active use if it is uncertain whether adequate laboratory ventilation will be maintained when the hood is off.

In the laboratory the chemical fume hood is the primary means of controlling inhalation exposures. Hoods are designed to retain vapors and gases released within them, protecting the laboratory employee's breathing zone from the contaminant. This protection is accomplished by having a curtain of air move constantly through the face (open sash) of the hood. The face velocity should be approximately 100 linear feet per minute (fpm). Chemical fume hoods can also be used to isolate apparatus or chemicals that may present physical hazards to employees. The closed sash on a hood serves as an effective barrier to fires, flying objects, chemical splashes or spattering and small implosions and explosions.

When using a chemical fume hood keep the following principles of safe operation in mind:

The Facilities Services Department has a contract vendor that who tests the flow rate of each ducted hood annually. The target goal for each hood is 100 fpm flow rate. An inspection label indicating the date of the inspection, the inspector, and the sash height at which the target value of 100 fpm was achieved is attached to each hood at the time of the inspection by the vendor. If your hood has not been inspected and does not have a current sticker contact Facilities Services at 874-4060 and request an inspection. If the hood is not operating, make sure that the power switch is on. It is always a trade-off between energy

conservation and providing safe ventilation in the labs. In most labs the hoods should be left on at all times when chemicals are stored and utilized in the laboratory to ensure that fumes of hazardous chemicals are adequately exhausted and the laboratory functions as designed. Many laboratories rely on the draw of the hood to maintain the laboratory in negative pressure relative to the hallway. This assures that volatile fumes are exhausted rather than circulating throughout the building.

Laboratories should provide 6-10 air changes per hour to safely work with most chemicals. If there is a malfunction of a hood contact the Facilities Services Dispatcher at 874-4060 and report the problem so that repairs can be scheduled. A sign should be placed on the hood to indicate that it is "out of service". Work that needs to be conducted in the hood must be scheduled after the repairs are completed or an alternate hood must be used.

The user must follow the chemical manufacturer's or supplier's specific instructions for controlling inhalation exposures with ventilation (chemical fume hood) when using their products. These instructions are located on the products SDS and/or label. However, it should be noted that these ventilation recommendations are often intended for non-laboratory work environments and must be adapted to suit the laboratory environment, as well as the specific procedure or process.

The American Chemical Society recommends the following procedures for properly using ventilation with toxic chemicals:

- 1. When a Time Weighted Average (TWA) Threshold Limit Value (TLV) or Permissible Exposure Limit (PEL) value is less than 50 ppm or 100 mg/m³ (air concentration), the user of the chemical must use it in an operating fume hood, glove box, vacuum line or similar device, which is equipped with appropriate traps and/or scrubbers. Refer to Section 8 of the safety data sheet (SDS) for your chemical to determine the TLV or PELs. If no such devices are available, no work should be done with this chemical.
- 2. If a TLV, PEL, or comparable value is not available for that substance, review the animal or human median inhalation lethal concentration information, LC50, located in Section 11 of the SDS. If that value is less than 200 ppm or 2000 mg/m³, when administered continuously for one hour or less, then the chemical must be used in an operating fume hood, glove box, vacuum line or similar device, which is equipped with appropriate traps and/or scrubbers. If no such devices are available, no work should be done with this chemical.
- 3. Whenever laboratory handling of toxic substances with moderate or greater vapor pressures will likely exceed air concentration limits, laboratory work with such liquids and solids must be conducted in an operating fume hood, glove box, vacuum line or similar device, which is equipped with appropriate traps and/or scrubbers. If no such devices are available, no work should be done with this chemical. [Source: Developing a Chemical Hygiene Plan, Young, J.A., Kingsley, W.K and G.H. Wahl, ACS, 1990]

2.3.5.2 Commentary on the Use of Ductless Chemical Fume Hoods

Ductless chemical fume hoods (hoods which recycle air to the laboratory after passing it through a filter) are now being offered by a variety of manufacturers. Manufacturers claim that these devices are safe and extremely energy efficient because no air is exhausted from the laboratory. These systems typically have a particulate filter and/or a charcoal filter for the removal of organic vapors. These systems must be used with extreme caution.

The primary safety concern with these devices is their filtering mechanism. The correct filter must first be chosen for the chemical that will be used in the hood. There is no "universal" filter for all contaminants of concern. Additionally, charcoal filters are not 100% efficient at removing organic vapors. Thus, some organic vapor will always be returned to the laboratory atmosphere. Charcoal filters have a limited ability to adsorb organic vapors and become saturated in a matter of months. Most hoods do not have a method for detecting when the filters are saturated and breakthrough of organic vapors begins. Those that have monitors depend on non-specific chemical sensors, which will respond at different concentrations for different substances. Some substances will not be detected. Charcoal filter replacements are extremely expensive, and studies have shown that, when operated over several years, ductless hoods may actually be more expensive (as well as less protective) to operate than ducted hoods.

Applications where ductless chemical fume hoods might be appropriate include the control of particulate and nuisance odors. Ductless hoods should not be used to protect laboratory workers from toxicologically significant concentrations of hazardous chemicals. A careful assessment of the suitability for a particular project must be conducted before purchasing this type of hood. The user must provide the manufacturer with a list of the potential chemicals to be used in the ductless hood and their anticipated quantities of usage prior to purchase to determine the appropriate type of unit that should be purchased.

Where ductless hoods are installed their use must be monitored to ensure that usage does not change over time and that proper procedures are followed. The Principal Investigator/laboratory supervisor must maintain a run-time log as part of the laboratory documentation that indicates the type and quantity of chemical that has been used and its duration. The log should include a record of maintenance and cartridge change. In addition, a service contract should be purchased from the vendor to perform the annual hood certification and perform any needed maintenance. The run-time log will determine the appropriate information for the hazardous waste label that will be required for disposal of the filters. All hazardous waste disposal of the hood cartridges must be to an EPA-permitted facility. If the users' Department requests that the filter cartridges be disposed by EH&S the disposal cost may be charged back to the users' Department if frequent filter cartridge change is required or the chemical disposal presents special challenges and/or added costs.

2.3.5.3 Glove Boxes

The ventilation in a negative pressure glove box must be at least 2 volume changes/hour and the pressure must be at least 0.5 inches of water. Thoroughly check a positive pressure glove box for leaks before each use. In either case if the exit gases are hazardous, they should be trapped or passed through an appropriate filter before they are released into the hood.

2.3.5.4 Eyewashes and Safety Showers

Whenever chemicals have the possibility of damaging the skin or eyes, an emergency supply of water must be available. All laboratories where hazardous chemicals are handled and could contact the eyes or skin resulting in injury must have readily available access to eyewash stations and safety showers. As with any safety equipment, these can only be useful if they are accessible and operational, therefore:

- Keep all passageways to the eyewash and shower clear of any obstacle (even a temporarily parked chemical cart).
- Eyewashes must be checked weekly by laboratory personnel to be certain that water flows through them. If the eyewashes are plumbed to a drain allow them to run for several minutes once per week to clear out the supply lines, remove dust and prevent bacterial contamination. Eyewashes should have protective covers that come off when the water is turned on.

- Showers should be checked routinely to assure that access is not restricted and that the pull chain is within reach.
- The water flow through the safety showers must be tested to ensure sufficient flow (approximately 30 gallons per minute). Safety showers (without floor drains) must be inspected and flushed by EH&S. Any known malfunction of safety showers and eye washes should be reported promptly to EH&S and the Facilities Services Dispatcher at 874-4060.
- Many departments have had success with the use of eyewashes that attach directly to the laboratory faucet. These are very reasonably priced and easy to install. EH&S can assist in locating product information.
- At the start of each semester, the PI (or their designee) is responsible for showing lab users the location of the eyewash and safety shower and directions on how to use. PIs should contact SH&S if they are unsure of the operation of their eyewash or safety shower.

2.3.5.5 Fire Safety Equipment

Fire safety equipment must be readily accessible to the laboratory and must include an appropriate size and type of fire extinguisher (generally type ABC) for the type and quantity of chemicals stored in the laboratory. Other equipment may include fire hoses, fire blankets, and automatic extinguishing systems. Fire extinguishers should be located within 35 feet of high hazard laboratories and 70 feet for other laboratories. NFPA Guide 10 provides specifications for portable fire extinguishers. If special fire extinguishers are required, such as Type D that are used for sodium, potassium and lithium fires, then the cost of these units must be provided by the Principal Investigator or Department. Each fire extinguisher must have a current inspection sticker. If you have questions about fire extinguishers contact URI Fire and Life Safety at 874-7994 or EH&S.

2.4 Chemical Procurement, Distribution, and Storage

2.4.1 Procurement

Before a new substance that is known or suspected to be hazardous is received, those individuals who will handle it must have information and training on proper handling, storage, and disposal. It is the responsibility of the Principal Investigator to ensure that the laboratory facilities in which the substance will be handled are adequate and that those who will handle the substance have received the proper training. The necessary information on proper handling of hazardous substances can be obtained from the Safety Data Sheets, which are provided by the vendor. Because storage in laboratories is restricted by fire and building codes to small containers, order small-container lots to avoid hazards associated with repackaging. When planning an experiment assess whether hazards can be reduced by substituting a similar but less dangerous chemical. Ownership of chemicals involves responsibility from "cradle to grave". By purchasing the smallest quantity that is feasible money may be saved in two ways – the acquisition cost may be less and the disposal cost of any chemical remaining at the end of the experiment will be greatly reduced. In addition, the storage of smaller quantities of chemicals takes less space in the laboratory and reduces the overall risk. Also, a fresh reagent may produce better experimental results than one that has been stored for a long time.

No container should be accepted from a vendor without an adequate identifying label, which must include the following elements: Product Identifier, Supplier Information, Precautionary Statements, Hazard Pictograms, Signal Word, and Hazard Statement as shown on the sample label below.

	SAMPLE LABEL
CODE Produce Product Name Produce Identifi	Hazard Pictograms
Company Name	
Keep container tightly closed. Store in a cool, well-ventilated place that is locked.	Signal Word Danger
Keep away from heat/sparks/open flame. No smoking. Only use non-sparking tools. Use explosion-proof electrical equipment. Take precautionary measures against static discharge. Ground and bond container and receiving equipment. Do not breathe vapors. Wear protective gloves. Do not eat, drink or smoke when using this product. Wash hands thoroughly after handling. Dispose of in accordance with local, regional, national, international regulations as specified.	Highly flammable liquid and vapor. May cause liver and kidney damage. Hazard Statements Precautionary Statements Supplemental Information
In Case of Fire: use dry chemical (BC) or Carbon Dioxide (CO ₂) fire extinguisher to extinguish.	Directions for Use
First Aid If exposed call Poison Center. If on skin (or hair): Take off immediately any contaminated clothing. Rinse skin with water.	Fill weight: Lot Number: Gross weight: Fill Date: Expiration Date:

2.4.2 Moving Chemicals

When hand carrying open containers of hazardous chemicals or unopened containers with corrosive, highly acutely or chronically toxic chemicals, place the container in a secondary container or a bucket with a screw-on lid. Rubberized buckets and plastic bottle carriers are commercially available and provide both secondary containment as well as "bump" protection. If several bottles must be moved at once, the bottles should be transported on a small cart with a substantial rim to prevent slippage from the cart. Wherever available, a freight elevator should be used to transport chemicals from one floor to another. If a passenger elevator must be used then the number of passengers should be restricted to necessary personnel. For special applications such as field work or work on a research vessel it is recommended that the chemicals be in unbreakable containers. It is possible to buy vinyl-coated "safety bottles", of reagents.

2.4.3 Chemical Storage in the Laboratory

Carefully read the label before storing a hazardous chemical. The SDS will provide any special storage information, as well as information on incompatibilities. To minimize eye injuries do not store chemicals, especially liquids, above the eye level of the shortest person in the lab. <u>Do not store unsegregated chemicals in alphabetical order</u>. <u>Do not store incompatible chemicals in close proximity to each other</u>. <u>Chemicals should not be stored on the floor or near sinks or in sinks</u>. Contact EH&S with any questions regarding chemical storage and compatibility.

- Use approved storage containers and safety cans for flammable liquids. Approved storage containers, safety cans and storage cabinets must be independently certified by UL or FM Global to meet OSHA and NFPA regulations. It is preferable to store flammable chemicals in flammable storage cabinets. Flammable chemicals requiring refrigeration should be stored only in the refrigerators and freezers specifically designed for flammable storage. These are referred to as UL rated flammable refrigerators/freezers or "explosion-proof" refrigerators.
- Do not store chemicals on bench tops or in hoods if the chemicals are not in active use. Clutter presents opportunities for accidents.
- Liquid chemicals (particularly corrosives or solvents) should not be stored above the eye level of the shortest person in the laboratory.
- Use secondary containers, such as chemically resistant trays or outer containers, to segregate and isolate especially hazardous chemicals such as carcinogens, concentrated acids, or bases.
- Avoid exposure of chemicals to heat sources (especially open flames) and direct sunlight. <u>Be aware that many buildings at URI are heated by steam heat</u>. Do not store chemicals or put chemical storage cabinets next to the steam pipes. If your chemicals are stored in such cabinets, you may need to notify Facilities Operations that you need to be placed on the Emergency Notification list. In may be necessary to open windows or use fans if the steam distribution system shuts down during an extended power outage. To prevent the buildings from freezing in the winter the pneumatic valves are open when the power is off. In an extended power outage ventilation of individual labs storing highly volatile/flammable may be required.
- All containers of chemicals should be dated when they are received and again when they are opened so that their suitability and safety for use can be assessed. Some chemicals such as peroxide formers become unstable and potentially explosive if they are stored for more than a few months and need to be tested to minimize the risk of an in-lab explosion.
- Conduct periodic inventories of chemicals stored in the laboratory (at least annually) and dispose of old or unwanted chemicals promptly. Also assess the condition of caps and containers and discard those that are in unsafe condition.

• Assure all containers are properly labeled. Don't forget to label bottles stored in refrigerators and freezers.

Separate hazardous chemicals in storage in the general categories as indicated in the following table:

General Categories	Common Laboratory Chemicals
Compatible Organic Bases	• Ethanolamine • Isopropylamine • Triethanolamine •
	Triethylamine • TEMED (Tetramethylethylenediamine) •
	Diaminobenzidine (DAB)
Compatible Organic Acids	Butyric acid Citric acid monohydrate Formic acid Glacial
	acetic acid (also store with flammables if segregated) • 4-
	Morpholinepropanesulfonic acid (MOPS buffer) • Propionic acid
Not Intrinsically Reactive or Flammable or Combustible	 Acrylamide, bis-acrylamide Agarose Ammonium thiosulfate
(solids, store separately above liquids)	Chloroquine diphosphate • Coomassie brilliant blue • Dextrose •
	Dithiothreitol • Guanidine hydrochloride • Magnesium chloride •
	Methotrexate • Sodium citrate • Sodium phosphate, monobasic •
	Potassium chloride • Potassium ferricyanide • X-Gal (5-Bromo-4-
	chloro-3- indolyl-B-D-galactopyranoside)
Non-Reactive Flammables and Combustibles (including	Alcohols Acetaldehyde Acetone Acetonitrile Amyl acetate
solvents)	Benzene • Carbon disulfide • Cyclohexane • Dichloromethane •
	Diethyl pyrocarbonate • Dimethylformamide • Dimethyl sulfate •
	Dimethylsulfoxide (DMSO) • Dioxane • Ethyl ether • Ethyl acetate •
	Formaldehyde, 37% • Formamide • Hexane • Hydrazine • Isoamyl alcohol • β-Mercaptoethanol • Methyl ethyl ketone • Methylene
	chloride • Paraformaldehyde solid • Phenol • Piperidine • Propanol
	Sodium dodecyl sulfate (SDS) Tetrahydrofuran Toluene
	Xylenes
Compatible Inorganic Bases	Ammonium hydroxide • Potassium hydroxide • Sodium hydroxide
	solutions
Compatible Oxidizers, including Peroxides	• Ammonium nitrate • Ammonium perchlorate • Ammonium
	persulfate • Benzoyl peroxide, wet • tert-Butyl hydroperoxide •
	Calcium hypochlorite • Chlorosulfonic acid • Chromic acid • Fuming
	nitric acid • Hydrogen peroxide, 30% • Isoamyl nitrite • Potassium
	chlorate • Potassium dichromate • Potassium permanganate •
	Silver nitrite • Sodium chlorate • Sodium chlorite • Sodium
	hypochlorite solution (bleach)
Compatible Inorganic Acids (not including Oxidizers or Combustibles)	Hydrochloric acid Nitric acid Phosphoric acid Sulfuric acid
Not Intrinsically Reactive or Flammable or Combustible (liquids)	Chloroform • Isoflurane
Incompatible with ALL other storage groups	Sodium azide Picric acid 10-40% water
Compatible Pyrophoric and Water Reactive Materials	Acetyl chloride • Lithium aluminum hydride, other metal hydrides
-	• Phosphorus pentachloride • Silanes such as Silane gas,
	Dimethyldichlorosilane • Sodium • Sodium hydride • Toluene 2,6-
	diisocyanate
Compatible Explosive or other highly unstable materials	Ammonium picrate, dry Benzoyl peroxide, 97% Dinitrophenol
	 Mercury fulminate Nitroglycerin Picric acid, dry
	Trinitrotoluene (TNT)

Related and Compatible Storage Groups

2.4.3.1 Chemical Storage - Chemical Stability

Stability refers to the susceptibility of a chemical to dangerous decomposition. The label and SDS will indicate if a chemical is unstable.

Special note: peroxide formers - Ethers, liquid paraffins, and olefins may form peroxides on exposure to air and light. Peroxides are extremely sensitive to shock, sparks, or other forms of accidental ignition and may be even more sensitive than primary explosives such as TNT. Since these chemicals are generally packaged in an air atmosphere, peroxides can form even though the containers have not been opened. Unless an inhibitor was added by the manufacturer, sealed containers of ethers should be discarded after one (1) year. Opened containers of ethers should also be discarded within one (1) year of opening unless a shorter time is specified on the label or SDS. All such containers should be dated upon receipt and upon opening. See Section 3.3.4 for a list of materials that may form explosive peroxides and Section 3.3.1 for Special Handling Procedures for these chemicals.

2.4.3.2 Chemical Storage - Incompatible Chemicals

Certain hazardous chemicals should not be mixed or stored with other chemicals because a severe reaction can take place or an extremely toxic reaction product can result. The label and SDS will contain information on incompatibilities. The following table contains examples of incompatible chemicals.

List of Some Incompatible Laboratory Chemicals

CHEMICAL	KEEP OUT OF CONTACT WITH:
Acetic Acid	Chromic acid, nitric acid hydroxyl compounds, ethylene glycol, perchloric acid, peroxides, permanganates
Acetone	Concentrated nitric and sulfuric acid mixtures
Acetylene	Chlorine, bromine, copper, fluorine, silver, mercury
Alkali Metals	Water, carbon tetrachloride or other chlorinated hydrocarbons, carbon dioxide, the halogens
Ammonia, anhydrous	Mercury, chlorine, calcium hypochlorite, iodine, bromine, hydrofluoric acid
Ammonium Nitrate	Acids, metal powders, flammable liquids, chlorates, nitrites, sulfur, finely divided organic or combustible
	materials
Aniline	Nitric acid, hydrogen peroxide
Arsenical	Any reducing agent materials
Azides	Acids
Bromine	Same as chlorine
Calcium Oxide	Water
Carbon (activated)	Calcium hypochlorite, all oxidizing agents.
Carbon tetrachloride	Sodium
Chlorates	Ammonium salts, acids, metal powders, sulfur, finely divided organic or combustible materials
Chromic Acid	Acetic acid, naphthalene, camphor, glycerin, turpentine, alcohol, flammable liquids in general
Chlorine	Ammonia, acetylene, butadiene, butane, methane, propane, (or other petroleum gases), hydrogen, sodium
	carbide, turpentine, benzene, finely divided metals
Chlorine Dioxide	Ammonia, methane, phosphine, hydrogen sulfide
Copper	Acetylene, hydrogen peroxide
Cumene Hydroperoxide	Acids, organic or inorganic
Cyanides	Acids
Flammable Liquids	Ammonium nitrate, chromic acid, hydrogen peroxide, nitric acid, sodium peroxide, halogens
Hydrocarbons	Fluorine, chlorine, bromine, chromic acid, sodium peroxide
Hydrocyanic Acid	Nitric acid, alkali
Hydrofluoric Acid	Ammonia, aqueous or anhydrous
Hydrogen Peroxide	Copper, chromium, iron, most metals or their salts, alcohols, acetone, organic materials, aniline, nitromethane,
nyulogen i cloxide	flammable liquids, oxidizing gases
Hydrogen Sulfide	Fuming nitric acid, oxidizing gases, acetylene, ammonia (aqueous or anhydrous), hydrogen
Hypochlorites	Acids, activated carbon
lodine	Acetylene, ammonia (aqueous or anhydrous), hydrogen
Mercury	Acetylene, fulminic acid, ammonia
Nitrates	Sulfuric acid
Nitric Acid (concentrated)	Acetic acid, aniline, chromic acid, hydrocyanic acid, hydrogen sulfide, flammable liquids, flammable gases
Nitrites	Acids
Nitroparaffins	Inorganic bases, amines
Oxalic Acid	Silver, mercury
Oxygen	Oils, grease, hydrogen; flammable liquids, solids, or gases
Perchloric Acid	Acetic anhydride, bismuth and its alloys, alcohol, paper, wood
	Acids (organic or mineral), avoid friction, store cold
Peroxides, organic	
Phosphorus (white) Potassium	Air, oxygen, alkalies, reducing agents Carbon tetrachloride, carbon dioxide, water
	Carbon tetrachloride, carbon dioxide, water Sulfuric and other acids
Potassium Chlorate	
Potassium Permanganate	Glycerin, ethylene glycol, benzaldehyde, sulfuric acid
Selenides	Reducing agents
Silver	Acetylene, oxalic acid, tartaric acid, ammonium compounds
Sodium Sodium nitrito	Carbon tetrachloride, carbon dioxide, water
Sodium nitrite	Ammonium nitrate and other ammonium salts
Sodium Peroxide	Ethyl or methyl alcohol, glacial acetic acid, acetic anhydride, benzaldehyde, carbon disulfide, glycerin, ethylene
C IC sta Astal	glycol, ethyl acetate, methyl acetate, furfural
Sulfuric Acid	Potassium chlorate, potassium perchlorate, potassium permanganate (or compounds with similar light metals,
T all a data a	such as sodium, lithium, etc.)
Tellurides	Reducing agents

(From Manufacturing Chemists' Association, Guide for Safety in the Chemical Laboratory, pp. 215-217.)

2.5 Chemical Spills and Accidents

2.5.1 General Information

The Principal Investigator should anticipate the types of chemical spills that may occur in his/her laboratory and obtain the necessary equipment (spill kits and personal protective equipment) to respond to a minor spill. Learn how to safely clean up minor spills of the chemicals you use regularly. The SDS contains special spill clean-up information and should be consulted. **Chemical spills should only be cleaned up by knowledgeable and experienced personnel.**

If the spill is too large for you to handle, is a threat to personnel, students or the public, or involves a highly toxic, or reactive chemical, evacuate and call for assistance immediately:

FOR ALL EMERGENCIES call 911. For assistance with spill cleanup (non-emergencies), contact URI dispatch during the day and after hours at 874-4910.

The following compounds are very hazardous. You should not try to clean up any significant spill of these materials yourself.

-Aromatic amines

- -Bromine
- -Carbon disulfide
- -Cyanides
- -Ethers and other 1A flammable solvents
- -Hydrazine
- -Nitriles
- -Nitro compounds
- -Organic Halides

2.5.2 Cleaning Up Chemical Spills

The following sections are included for your reference only. If you are unsure how to proceed evacuate the area immediately and call EH&S for assistance.

If you are cleaning up a small spill yourself, make sure that you are aware of the hazards associated with the materials spilled, have adequate ventilation (open windows, chemical fume hood on) and proper personal protective equipment (minimum - gloves, goggles, and lab coat). Consider all residual chemical and cleanup materials (adsorbent, gloves, etc.) as hazardous waste. Place these materials in sealed containers and store in the designated Satellite Accumulation Area. Place label on the container, identifying the chemical spilled. If there are still chemical odors or volatiles substances such as mercury associated with the clean-up materials it is prudent to place them in a chemical fume hood. Submit a request to EH&S to arrange a hazardous waste pick-up.

2.5.3 Minor Chemical Spill

- Alert people in the immediate area of the spill.
- Increase ventilation in the area of the spill (open windows, turn on hoods).
- Wear protective equipment, including safety goggles, gloves, long-sleeve lab coat and closed toe shoes.
- Avoid breathing vapors from the spill.
- Use the appropriate kit to neutralize and absorb inorganic acids and bases.
- Collect the residue, place in a leak-proof container, and dispose as hazardous chemical waste.
- For other chemicals, use appropriate kit or absorb spill with spill pads or dry sand.

- Collect residue, place in container, and dispose as hazardous chemical waste.
- Clean and decontaminate the spill area with an appropriate cleaning material.

If a laboratory contains hazardous chemicals or infectious agents, then a chemical and/or biological spill kit must be available and fully stocked. EH&S also has spill kits specific to mercury and hydrofluoric acid spills (contact EH&S for one of these kits or assistance in cleaning one of these spills). Other items that the Principal Investigator should stock in the spill kit are the listed below. If flammable chemicals are used in the lab then non-sparking implements should be used.

Chemical Spill Kit	Biological Spill Kit
Dustpan and brush or small broom	Absorbent
Chemically resistant gloves, nitrile, neoprene	Biologically resistant gloves, nitrile, latex
Safety glasses/goggles	Disinfectant
Tongs	Paper Towels
Absorbent	Safety glasses/goggles
	Tongs

2.5.4 Major Chemical Spill

- Alert people in the laboratory to evacuate.
- Call 911 for all emergencies.
- Attend to injured or contaminated persons and remove them from exposure if you can do so safely.
- If spilled material is flammable, turn off ignition and heat sources. Place a vapor retarding device (e.g., plastic bag or absorbent) over spilled material to keep substance from volatilizing. Close doors to the affected area, if possible, as you evacuate.
- Have a person with knowledge of the incident and laboratory available to answer questions from responding emergency personnel.

2.5.5 Mercury Spills and Hydrofluoric Acid Spills

- Use a mercury spill kit or hydrofluoric acid spill kit and follow the manufacturer's directions for a small spill (contact EH&S or your PI to obtain mercury or HF spill kits).
- Place the clean-up materials in a labeled container and label as hazardous waste. Contact EH&S to arrange a pick-up. Do not attempt to clean up a large spill. If you have a mercury spill that exceeds the quantity found in a normal laboratory thermometer contact EH&S. Never use a broom or vacuum cleaner to clean up a mercury spill.

2.6 Personal Chemical Contamination and Injury

2.6.1 General Information

To summon an ambulance, dial 911. Report the location of the injured person.

- Know the locations of the nearest safety shower and eye wash station and how to use them.
- Report all incidents and injuries to your supervisor.
- If an individual is contaminated or exposed to a hazardous material in your laboratory do what is necessary to protect their life and health as well as your own. Determine what substance the individual was exposed to. The SDS will contain special first aid information. Send a copy of the SDS to the hospital with the patient.
- Do not move an injured person unless they are in further danger (from inhalation or skin exposure).

• Do not attempt CPR if you think the victim has been exposed to a hazardous chemical. Without special training and personal protective equipment, you could ingest or be exposed to the same hazardous material from the victim.

2.6.2 Chemicals Spills on the Body

- Put on personal protective equipment such as gloves and safety goggles to avoid contaminating yourself while assisting the injured person.
- Quickly assist the victim to remove all contaminated clothing and footwear.
- Immediately flood the affected body area with water for at least 15 minutes. Remove jewelry to facilitate removal of any residual material that may be trapped next to the skin.
- Wash off chemicals with water only. Do not use neutralizing chemicals, creams, lotions or salves.
- Get medical attention promptly. Call 911 if an ambulance is required.
- Provide the physician with the chemical name and a copy of the SDS.

It should be noted that some chemicals (phenol, aniline) are rapidly adsorbed through the skin. If a large enough area of skin is contaminated an adverse health effect (systemic toxicological reaction) may occur immediately to several hours after initial exposure depending on the chemical. Seek medical attention immediately by calling 911 after washing the material off the skin for exposure to these chemicals. If the incident involves hydrofluoric acid (HF), rinse with copious amounts of water and seek immediate medical attention. All labs using hydrofluoric acid must stock the calcium gluconate antidote and HF spill kit.

2.6.3 Chemical Splash in the Eye

- Immediately irrigate the eyeball and inner surface of eyelid with copious amounts of cool water for at least 15 minutes. Use eyewash or other water source. Forcibly hold eyelids open to ensure effective wash. If there is a second person in the lab have them assist in keeping the eye open for irrigation. Reflex action will cause the individual to try to close their eye, thus trapping the chemical in the eye.
- FOR CONTACT LENSE WEARERS: initially rinse eyes for one minute, remove contact lenses, then continue rinsing eyes and the inner surface of the eyelid for at least 15 minutes.
- Get medical attention promptly. Call 911 for medical attention.
- Please be aware that caustic burns may cause as much or more damage to the eye than acid burns.

2.6.4 Ingestion of Hazardous Chemicals

- Identify the chemical ingested.
- Call 911 for medical attention.
- Cover the injured person to prevent shock.
- Provide the ambulance crew and physician with the chemical name and any other relevant information. If possible, send the container, SDS or the label with the victim.
- Call the Poison Control Center (24/7 phone number) for additional information: (800) 222-1222.

2.6.5 Inhalation of Smoke, Vapors and Fumes

- Evacuate immediately if smoke is seen or strong fumes are present.
- Call 911 immediately for police, fire or ambulance. Be prepared to report exact location.
- Anyone overcome with smoke or chemical vapors or fumes should be removed to uncontaminated air and treated for shock.

• Do not enter the area if you expect that a life-threatening condition still exists such as oxygen depletion, explosive vapors or highly toxic gases (cyanide gas, hydrogen sulfide, nitrogen oxides, carbon monoxide)

2.6.6 Burning Chemicals on Clothing

- Call 911 immediately for police, fire or ambulance. Be prepared to report exact location.
- Extinguish burning clothing by dousing the victim with cold water (use an emergency shower if it is immediately available) or by using the drop-and-roll technique.
- Remove contaminated clothing; however, be careful to avoid further damage to the burned area.
- Remove heat with cool water or ice packs until tissue around burn feels normal to the touch.
- Cover injured person to prevent shock.

2.6.7 Actions to be Avoided During Emergencies

- Do not force any liquids into the mouth of an unconscious person.
- Do not handle emergencies alone, especially without notifying someone that the accident has occurred.
- Do not linger at the accident scene after you have provided information to the emergency responders unless you are requested to do so.

2.7 Fire and Fire Related Emergencies

If you discover a fire or fire-related emergency such as abnormal heating of material, a flammable gas leak, a flammable liquid spill, smoke, or odor of burning, immediately follow these procedures:

- Evacuate the area. Activate the building alarm (fire pull station). If not available or operational, verbally notify people in the building.
- Call 911 and report location.
- Isolate the area by closing the windows and doors (if safe to do so) and evacuate the building.
- Shut down equipment in the immediate area if it is possible and safe to do so quickly while you are leaving.
- Use a portable fire extinguisher to:
 - assist oneself to evacuate;
 - assist another to evacuate.

Provide the fire/police teams with the details of the problem upon their arrival, including hazard information (chemicals or equipment in use) that you might know may be essential for the safety of the emergency responder.

What to Do if the Fire Alarms are Ringing in Your Building:

- Evacuate the building and stay out until notified to return.
- Move upwind from the building and stay clear of streets, driveways, sidewalks and other access ways to the building.
- If you are a supervisor, try to account for your staff, keep them together and report any missing persons to the emergency personnel at the scene.
- As part of each lab's Emergency Action Plan, Pre-arrange an assembly point so that it can be determined that everyone has left the laboratory and building safely.

2.8 Chemical Hazardous Waste Disposal Program

Laboratory chemical waste must be handled according to EPA and RI DEM regulations.

The University's hazardous waste management practices are designed to ensure maintenance of a safe and healthful environment for laboratory employees and the surrounding community without adversely affecting the environment. This is accomplished through regular removal of chemical hazardous waste from University facilities and disposal of these wastes in compliance with local, state, and federal regulations. Any questions about hazardous waste management should be directed to EH&S. To dispose hazardous waste laboratory users must fill out a "Hazardous Waste Pickup Request" form found on the EH&S web page: https://web.uri.edu/EH&S/hazardous waste/. This form can either be submitted using the online form or downloaded and filled out in Word or by hand. Once the form is filled out, submit by email to **srm@etal.uri.edu**.

2.9 Chemical Inventory

Principal Investigators should maintain an accurate chemical inventory. If your area has not yet been barcoded and entered in the University's computerized inventory system please compile an inventory of all the chemicals in your laboratory using the Excel inventory template available from EH&S. An inventory must be submitted annually to EH&S for all areas storing chemicals and hazardous materials. Principal Investigators who have never submitted an inventory to EH&S should prepare one now. All subsequent inventories are due on July 1 of each year (this only applies to labs in which EH&S staff does not prepare the chemical inventory). Inventories created in a spreadsheet or database are easy to maintain. The Excel spreadsheet should be submitted electronically to **srm@etal.uri.edu**.

Principal Investigators are responsible for keeping their inventories updated (contact EH&S to request a copy of the chemical inventory for your specific lab). New chemicals can be added to EH&S electronic inventory database by contacting EH&S. When chemicals that have been bar-coded are disposed, the bar-code label, or the bar-code number should be entered onto the Hazardous Waste Pick-up Request Form. For assistance in completing the forms please contact EH&S.

The guidelines presented below for culling inventory shall be followed as presented in *Prudent Practices in the Laboratory*, (National Research Council, 1995):

- Consider disposing of materials that you don't expect to use within a reasonable period (~2 years). Stable, relatively nonhazardous substances may have indefinite shelf lives; a decision to retain them in storage should take into account their economic value, condition of container (plastic and metal containers tend to deteriorate over time), availability, and storage costs.
- Make sure that deteriorating containers, or containers in which evidence of a chemical change in the contents is apparent (e.g., appearance of peroxide crystals in a bottle of ether), are inspected and handled by someone experienced in the possible hazards inherent in such situations.
- Dispose of or recycle chemicals before the expiration date on the container.
- Replace deteriorating labels before information is obscured or lost.
- Because many odoriferous substances will make their presence known despite all efforts to contain them, aggressively purge such items from storage and inventory.
- Aggressively cull the inventory of chemicals that require storage at reduced temperature in environmental rooms or refrigerators. Because these chemicals may include air- and moisture-sensitive materials, they are especially prone to problems that can be exacerbated by the effects of condensation.

Dispose of or distribute all hazardous chemicals when the PI or laboratory supervisor leaves or transfer to another laboratory. URI has a strict policy regarding laboratory vacancies (in the case of a Principal Investigator retiring, leaving URI for another position, or transferring to another laboratory). The University's Policy on Laboratory Move-Ins and Cleanouts requires faculty members and research investigators to work with EH&S to coordinate management of chemical, biological, and/or radiological materials when moving into or out of, or transitioning responsibility for, laboratory spaces containing such hazardous materials. EHS must be notified a minimum of four weeks prior to the PI leaving the laboratory. Failure to maintain a chemical inventory free from expired, unlabeled, unknown chemicals and chemicals that may require special handling (e.g., peroxide forming chemicals that have formed crystals) may result in the department covering the cost for part of the laboratory cleanout. Refer to the <u>URI's Laboratory Move-In and Cleanout Policy</u>, <u>URI's Move-In and Cleanout Procedures</u>, and the mandatory <u>Laboratory Clearance Form</u>, which must be filled out and submitted to EHS prior to vacating the lab.

Chapter 3.0 Guidelines for Working with Chemicals of Specific Hazard Classes

3.1 Flammable Liquids

Flammable liquids are among the most common of the hazardous materials found in laboratories. They are usually highly volatile (have high vapor pressures at room temperature) and their vapors, mixed with air at the appropriate ratio, can ignite and burn. By definition, the lowest temperature at which they can form an ignitable vapor/air mixture (the flash point) is less than 37.8° C (100° F) and for several common laboratory solvents (ether, acetone, toluene, acetaldehyde) the flash point is well below that. As with all solvents, their vapor pressure increases with temperature and, therefore, as temperatures increase they become more hazardous.

Flammable liquids may form flammable mixtures in either open or closed containers or spaces (such as refrigerators), when leaks or spills occur in the laboratory, and when heated.

Strategies for preventing ignition of flammable vapors include removing all sources of ignition or maintaining the concentration of flammable vapors below the lower flammability limit by using local exhaust ventilation such as a hood. The former strategy is more difficult because of the numerous ignition sources in laboratories. Ignition sources include open flames, hot surfaces, operation of electrical equipment, and static electricity. Older style hot plates should not be used with flammable materials because the unit may spark as the unit is activated to maintain temperature. Newer style hot plates are sealed units.

The concentrated vapors of flammable liquids may be heavier than air and can travel away from a source a considerable distance (across laboratories, into hallways, down elevator shafts or stairways). If the vapors reach a source of ignition a flame can result that may flash back to the source of the vapor. The danger of fire and explosion presented by flammable liquids can usually be eliminated or minimized by strict observance of safe handling, dispensing, and storing procedures. This includes grounding and bonding of containers prior to dispensing.

3.1.1 Special Handling Procedures

- While working with flammable liquids you should wear gloves, protective glasses or goggles, long sleeved lab coats and closed toe shoes. Wear goggles if dispensing solvents or performing an operation that could result in a splash to the face. If splash risk is high wear a face shield in addition to goggles.
- Large quantities of flammable liquids should be handled in a chemical fume hood or under some other type of local exhaust ventilation. Five-gallon containers must be dispensed to smaller containers in a hood or under local exhaust ventilation.
- When dispensing flammable solvents into small storage containers, use metal containers or safety cans or approved plastic containers with static dissipation devices (avoid glass containers).
- Make sure that metal surfaces or containers through which flammable substances are flowing (includes dispensing of flammable liquids from big containers to smaller ones) are properly grounded, discharging static electricity. Free flowing liquids generate static electricity which can produce a spark and ignite the solvent. A spark between two bodies occurs when there is a poor electrically conductive path between them. <u>Bonding</u> is done to eliminate a difference in potential between objects for example, between a 55-gallon drum and a 5 gallon can. <u>Grounding</u> is done to eliminate a difference in potential between an object and the ground. Class I liquids shall not be dispensed into containers unless the nozzle and container are electrically interconnected. [See 29CFR 1910.106(e)(6)(ii)] Buss

bars are the main source to ground in dispensing areas. Typically, busbars are copper wires wired directly to the ground grid (earth ground). Contact the electrical shop at Facilities Services if you have 55-gallon drums that require the installation of busbars for grounding purposes.

- Large quantities (five gallons) of flammable liquids must be handled in areas free of ignition sources (including spark emitting motors and equipment) using non-sparking tools. Remember that vapors may be heavier than air and can travel to a distant source of ignition.
- Never heat flammable substances by using an open flame. Instead use any of the following heat sources: steam baths, water baths, oil baths, heating mantles or hot air baths. Do not distill flammable substances under reduced pressure.
- Store flammable substances away from ignition sources. The preferred storage location is in flammable storage cabinets. If no flammable storage cabinet is available store these substances in a ventilated cabinet under the hood or bench, if available. Five-gallon containers should only be stored in flammable storage cabinets or in a storeroom with a high ventilation rate. You can also keep the flammable liquids inside the hood for a short period of time. Long-term storage in the chemical fume hood is not recommended because it reduces hood performance by obstructing air flow and reducing working area in the hood. Note that flammable substances should <u>never</u> be stored in a refrigerator or freezer not rated for flammable materials. Off gassing of vapors can lead to an explosion when the refrigerator or freezer cycles on. The rating of the refrigerator or freezer should be posted on a sticker or tag on the outside or inside door. When in doubt, contact EH&S for assistance.
- The volume of flammable liquids stored in small containers (not including safety cans) in the open areas of laboratories (not in a flammable storage cabinet) should not exceed 10 gallons for class I, highly flammable liquids. Note: The storage of flammable liquids is regulated by 29 CFR 1910.106, OSHA's Flammable and Combustible Liquids Standard. A copy is available on the OSHA website. This standard is based on NFPA 30, Flammable and Combustible Liquids Code. The standard is designed to prevent fires and explosions from flammable and combustible liquids. To prevent these hazards the standard addresses the primary concerns of design and construction; ventilation; ignition sources, and storage. Additional regulations are found in NFPA 45: Standard on Fire Protection for Laboratories using Chemicals. A copy may be requested from EH&S. This standard provides the requirements for the storage of flammable and combustible liquids for sprinklered and non-sprinklered laboratories. It also discusses the requirements for construction and fire protection for laboratory units for sprinklered and non-sprinklered laboratories; life safety considerations; automatic sprinkler requirements; portable extinguishers; electrical equipment used in laboratories; emergency plans; laboratory ventilation systems, requirements for manifolding laboratory exhaust systems, as well as compressed and liquefied gases. NFPA codes are reviewed by the various states and adopted into the state and local building and fire codes.
- Never store glass containers of flammable liquids on the floor.
- Oxidizing and corrosive materials should not be stored near flammable liquids.
- Flammable liquids requiring cold storage must not be stored or chilled in domestic (household) refrigerators and freezers but must be in units specifically rated and designed for this purpose. These units are sealed to prevent sparking during operation. Each refrigerator, freezer or cooler must be prominently marked to indicate whether it meets the standards for safe storage of flammable liquids. Flammable liquids stored in refrigerators and freezers must be properly labeled with the chemical name and hazards. It is also prudent practice to add the owner's name and the date the item was placed in storage.

• If flammable liquids will be placed in ovens, make sure they are appropriately designed for flammable liquids (no internal ignition sources and/or vented mechanically). Make sure the autoignition temperature of the solvent is above the oven temperature or its internal elements.

3.2 Pyrophoric Chemicals

Pyrophoric chemicals will readily oxidize and ignite spontaneously in air. Therefore, users must demonstrate that they have the appropriate laboratory equipment, PPE, spill kits, disposal containers and training to use these materials safely. The PI <u>must</u> prepare an SOP and submit it to EH&S for review when using any pyrophoric chemicals. Below is a list of common laboratory pyrophoric chemicals:

- Grignard Reagents: RMgX where R= organic, example methyl; X= halogen, example Cl
- Metal alkyls and aryls, such as RLi, RNa, R₃Al, R₂Zn
- Metal Carbonyls such as Ni(CO)₄, Fe(CO)₅, Co₂(CO)₈
- Alkali metals such as NA, K
- Metal powders such as Al, Co, Fe Mg, Mn, Pd, Pt, Ti, Sn, Zn, Zr
- Metal hydrides such as NaH, LiAlH₄
- Nonmetal hydrides, such as B₂H₆ and other boranes, PH₃
- Phosphorus (white)

3.3 Highly Reactive Chemicals and High Energy Oxidizers

In general chemicals with the following functional groups are prone to instability:

- -OO (peroxide)
- -N₃ (azide)
- -NO₂ (nitro)
- -C-N=O (nitroso)
- -CN=N (diazo)
- -ONO₂ (nitrate ester)
- -N= (imino)
- -NNO₂ (nitro amine)
- -C<u>=</u>N (cyanides, nitriles)

Highly reactive chemicals include those that are inherently unstable and susceptible to rapid decomposition as well as chemicals that, under specific conditions, can react alone, or with other substances in a violent uncontrolled manner, liberating heat, toxic gases, or leading to an explosion. Reaction rates almost always increase dramatically as the temperature increases. Therefore, if heat evolved from a reaction is not dissipated, the reaction can accelerate out of control and possibly result in injuries or costly accidents.

Air, light, heat, mechanical shock (when struck, vibrated, or otherwise agitated), water, and certain catalysts can cause decomposition of some highly reactive chemicals, and initiate an explosive reaction. Hydrogen and chlorine react explosively in the presence of light. Alkali metals, such as sodium, potassium and lithium, react violently with water liberating hydrogen gas. Examples of shock sensitive materials

include acetylides, azides, organic nitrates, nitro compounds, and many peroxides. See 3.3.2 below for a list of shock sensitive chemicals.

Organic peroxides are a special class of compounds that have unusual stability problems, making them among the most hazardous substances normally handled in the laboratories. As a class, organic peroxides are low powered explosives. Organic peroxides are extremely sensitive to light, heat, shock, sparks, and other forms of accidental ignition; as well as to strong oxidizing and reducing materials. All organic peroxides are highly flammable. Typical examples of organic peroxides are methyl ethyl ketone peroxide (MEKP), 1,1-dihydroperoxy cyclohexane, tert-Butyl hydroperoxide, Di-*tert*-butyl peroxide, t-butyl perbenzoate, benzoyl peroxide, 1,1-di-t-butylperoxycyclohexane and peracetic acid.

Peroxide formers can form peroxides during storage and especially after exposure to air (once opened). Peroxide forming substances include aldehydes, ethers (especially cyclic ether), compounds containing benzylic hydrogen atoms, compounds containing the allylic structure (including most alkenes), vinyl and vinylidine compounds.

3.3.1 Special Handling Procedures

If you have any reason to suspect that a shock sensitive material is in a deteriorated condition or has peroxides at high concentrations do not move it. Isolate the item and post a warning sign. Contact EH&S immediately. The item may need removal by individuals who are trained to handle high-hazard materials. Example, dry picric acid.

- Before working with a highly reactive material or high-energy oxidizer, review available reference literature to obtain specific safety information. The proposed reactions must be discussed with the principal investigator or your supervisor. Standard operating procedures (SOPs) must be written and implemented before these types of experiments are performed.
- Always minimize the amount of material involved in the experiment; the smallest amount sufficient to achieve the desired result should be used. Scale-ups should be handled with great care, giving consideration to the reaction vessel size and cooling, heating, stirring and equilibration rates.
- Excessive amounts of highly reactive compounds should not be purchased, synthesized, or stored in laboratories.
- The key to safely handling reactive chemicals is to keep them isolated from the substances that initiate their violent reactions.
- Unused peroxides must be discarded as hazardous waste and not be returned to the original container.
- Do not work alone. All operations where highly reactive and explosive chemicals are used must be performed during the normal workday or when other employees are available either in the same laboratory or in the immediate area.
- Perform all manipulations of highly reactive or high-energy oxidizers in a chemical fume hood. Some factors to be considered in judging the adequacy of the hood include its size in relation to the reaction and required equipment, the ability to fully close the sash, and whether the sash is a shatter-proof material.
- Make sure that the reaction equipment is properly secured. Reaction vessels must be supported from beneath with tripods or lab jacks. Use shields or guards that are clamped or secured. If possible, use remote controls for controlling the reaction (including cooling, heating and stirring controls). These must be located either outside the hood or at least outside the shield.
- Handle shock sensitive substances gently, avoid friction, grinding, and all forms of impact.

- Glass containers that have screw cap lids or glass stoppers must <u>not</u> be used. Polyethylene bottles that have screw-cap lids may be used.
- Handle water-sensitive compounds away from water sources.
- Light-sensitive chemicals should be used in light-tight containers.
- Handle highly reactive chemicals away from the direct light, open flames, and other sources of heat.
- Oxidizing agents must only be heated with fiberglass heating mantles or sand baths.
- High-energy oxidizers, such as perchloric acid, must only be handled in a wash-down hood. The oxidizer could volatilize and potentially condense in the ventilation system. If there are organic materials in the hood an explosion could occur. Inorganic oxidizers such as perchloric acid can react violently with most organic materials including lubricating oils in equipment.
- When working with highly reactive compounds and high-energy oxidizers always wear the following personal protection equipment: long sleeved lab coats, gloves, closed toe shoes and protective glasses/goggles. During the reaction, a face shield long enough to give throat protection must be worn. A face shield or body shield should be worn in addition to protective eyewear based on the scale of the reaction.
- Labels on peroxide forming substances must contain the date the container was received, first opened and the initials of the person who first opened the container. The substances must be checked for the presence of peroxides before using, and every three months while in storage. This information must be documented using the <u>Peroxide Forming Chemical Evaluation Form</u>. Peroxide test strips are commercially available. If peroxides are found in amounts greater than 25 ppm, the container must be disposed of. The results of any testing shall be indicated on the container label. <u>EH&S reserves the right to dispose of ANY containers of peroxide forming substances that are missing dates (received and first opened), appears suspect, and/or missing quarterly peroxide testing results.</u>
- Peroxide forming substances that have been opened for more than one year must be discarded. Unopened, sealed containers of peroxide formers must also be discarded after one year unless an inhibitor was added by the manufacturer. Peroxide formers shall be tested for peroxide formation at a minimum of every three months.
- Never distill substances contaminated with peroxides.
- Never use a metal spatula with peroxides. Contamination by metals can lead to explosive decompositions.
- Store highly reactive chemicals and high-energy oxidizers in closed cabinets segregated from the materials with which they react and, if possible, in secondary containers. Do not store these substances above eye level or on open shelves.
- Store peroxides and peroxide forming compounds at the lowest possible temperature. If you use a refrigerator, make sure it is appropriately designed and rated for the storage of flammable substances. Contact EH&S with questions or to assist with determining whether the refrigerator in a laboratory is rated for flammable or oxidizing material.
- Store light-sensitive compounds in the light-tight containers.
- Store water-sensitive compounds away from water sources.

3.3.2 List of Shock Sensitive Chemicals

Shock sensitive refers to the susceptibility of the chemical to decompose rapidly or explode when struck, vibrated, or otherwise agitated. The following are examples of materials that can be shock sensitive:

Acetylides of heavy metals

Hexanitrodiphenylamine

Picryl chloride

Aluminum ophrite explosive Amatol Ammonal Ammonium nitrate Ammonium perchlorate Ammonium picrate Ammonium salt lattice Butyl tetryl Calcium nitrate Copper acetylide Cyanuric triazide Cyclotrimethylenetrinitramine Cyclotetramethylenetranitramine Dinitroethyleneurea Dinitroglycerine Dinitrophenol Dinitrophenolates Dinitrophenyl hydrazine Dinitrotoluene **Dipicryl sulfone** Dipicrylamine Erythritol tetranitrate Fulminate of mercury Fulminate of silver Fulminating gold Fulminating mercury Fulminating platinum **Fulminating silver** Gelatinized nitrocellulose Germane Guanyl nitrosamino Guanyl-tetrazene GuanyInitrosaminoguanylidenehydrazin e Heavy metal azides Hexanite

Hexanitrostilbene Hexogen Hydrazinium nitrate Hyrazoic acid Lead azide Lead mannite Lead mononitroresorcinate Lead picrate Lead salts Lead styphnate Trimethylolethane Magnesium ophorite Mannitol hexanitrate Mercury oxalate Mercury tartrate Mononitrotoluene Nitrated carbohydrate Nitrated glucoside Nitrated polyhydric alcohol Nitrogen trichloride Nitrogen tri-iodide Nitroglycerin Nitroglycide Nitroglycol Nitroguanidine Nitroparaffins Nitronium perchlorate Nitrourea Organic amine nitrates Organic nitramines Organic peroxides Picramic acid Picramide Picratol Picric acid

Picryl fluoride Polynitro aliphatic compounds Potassium nitroaminotetrazole Silver acetylide Silver azide Silver styphnate Silver tetrazene Sodatol Sodium amatol Sodium dinitro-orthocresolate Sodium nitrate-potassium Sodium picramate Styphnic acid Tetrazene Tetranitrocarbazole Tetrytol Trimonite Trinitroanisole Trinitrobenzene Trinitrobenzoic acid Trinitrocresol Trinitro-meta-cresol Trinitronaphtalene Trinitrophenetol Trinitrophloroglucinol Trinitroresorcinol Tritonal Urea nitrate

3.3.3 List of High Energy Oxidizers

The following are examples of materials that are powerful oxidizing reagents:

Ammonium perchlorate Ammonium permanganate Barium peroxide Bromine Calcium chlorate Calcium hypochlorite Chlorine trifluoride Chromium anhydride or chromic acid Dibenzoyl peroxide Fluorine Hydrogen peroxide Magnesium perchlorate Nitric acid Nitrogen peroxide Perchloric acid Potassium bromate Potassium chlorate

Potassium perchlorate Potassium peroxide Propyl nitrate Sodium chlorate Sodium chlorite Sodium perchlorate Sodium peroxide

3.3.4 List of Peroxide Formers

The following are examples of the materials commonly used in laboratories that may form explosive peroxides:

Acetal	Dimethyl ether
Cyclohexene	Dioxane
Decahydronaphthalene	Divinyl acetylene
Diacetylene	Ether
Dicyclopentadiene	Ethylene glycol dimethyl ether
Diethylether	Isopropyl ether
Diethylene glycol	Methyl acetylene

Sodium amide Tetrahydrofuran Tetrahydronaphthalene Vinyl ethers Vinylidene chloride

3.4 Piranha Solutions

Piranha solutions are used to remove organic residues from substrates, particularly in microfabrication labs. The traditional piranha solution is a 3:1 mixture of sulfuric acid and 30% hydrogen peroxide. The solution may be mixed before application or directly applied to the material, applying the sulfuric acid, followed by the peroxide. Piranha solutions are extremely energetic and may result in explosion or injury resulting from chemical and thermal burns if not handled with extreme caution. Piranha solutions may irritate the respiratory tract if vapor is inadvertently inhaled.

3.4.1 Special Handling Procedures

- Always use glass (Pyrex[®] or Kimax[®] are preferred) containers. The solution can degrade plastic containers causing failure of containment.
- Ensure all containers are properly labeled to identify those containing piranha acid solutions.
- Always mix the solution in the hood, utilizing the hood sash as a barrier between you and the solution. Wear appropriate PPE when handling piranha solutions or waste, including acid resistant lab coat and/or apron with sleeve covers, gloves (butyl), chemical splash goggles and face shield.
- Always add hydrogen peroxide to sulfuric acid while gently stirring. DO NOT add sulfuric acid to hydrogen peroxide.
- The hydrogen peroxide concentration should be kept under 30% and should NEVER exceed 50%.
- Piranha solution will become very hot with temperatures exceeding 100°C during preparation. Handle with care to avoid thermal burns.
- Do not mix piranha solution with incompatible materials such as organic acids, organic solvents, or other organic materials. Do not mix with bases (e.g., Photoresist). Mixing piranha with incompatible materials can lead to an explosion.
- Ensure all containers and substrates are rinsed and dried before coming in contact with piranha solutions. Piranha solution is intended to remove residues only.
- When submerging items in piranha baths, place items in the piranha solution slowly and carefully. The solution needs time to stabilize after each item is added. Apply piranha solution to substrates carefully as well.
- <u>NEVER</u> store freshly prepared piranha solution in a closed or partially closed container.
- After use, always allow piranha solution to react overnight in a labeled, open container within a fume hood prior to final disposal.

Piranha solution is only to be collected for disposal after it has fully reacted, cooled and the gases of reaction have had adequate time to dissipate. A clean, recycled sulfuric acid bottle is a good option for

disposal. Initially, add only a small amount of the solution to waste container to ensure that there are no residual materials in the container that may cause an adverse reaction. If no reaction is observed, continue to pour slowly. The bottle should be explicitly labeled as containing waste piranha solution (labels can be obtained by EH&S). DO NOT COMBINE ANY OTHER WASTE SOLUTION WITH SPENT PIRANHA SOLUTION. Store waste solution in a container equipped with a <u>vented</u> cap (vented caps can be obtained by the laboratory supply vendor or contacting EH&S).

3.5 Compressed Gases

Compressed gases are unique in that they represent both a physical and a potential chemical hazard (depending on the particular gas). Gases contained in cylinders may be from any of the hazard classes described in this chapter (flammable, reactive, corrosive, or toxic). Because of their physical state (gaseous), concentrations in the laboratory can increase instantaneously if leaks develop at the regulator or piping systems, creating the potential for a toxic chemical exposure, asphyxiant or a fire/explosion hazard. Often there is little or no indication that leaks have occurred or are occurring. Finally, the large amount of potential energy resulting from compression of the gas makes a compressed gas cylinder a potential rocket or fragmentation bomb if the tank or valve is physically broken. Secure all cylinders properly!

3.5.1 Special Handling Procedures

- The contents of any compressed gas cylinder should be clearly identified. No cylinder should be accepted for use that does not legibly identify its contents by name. Color-coding is not a reliable means of identification and labels on caps have no value as caps are interchangeable. Carefully read the label before using or storing compressed gas. The SDS will provide any special hazard information
- Transport gas cylinders using specially designed carts, one or two at a time only, while they are secured and capped. All gas cylinders should be capped and secured when stored. Use suitable racks, straps, chains or stands to support cylinders. All cylinders, full or empty, must be restrained and kept away from heat sources.
- <u>At no time</u> may any compressed gas cylinder be transported by private or State of Rhode Island vehicle. Contact the gas cylinder vendor to transport any cylinder that cannot be transported <u>solely</u> via a cylinder hand truck.
- Store the minimum number of cylinders possible in your laboratory.
- Empty or unwanted cylinders must be returned to the vendor promptly.
- Use only Compressed Gas Association standard combinations of valves and fittings for compressed gas installations. Always use the correct pressure regulator. Do not use a regulator adaptor. The use of incompatible regulators or fittings may cause an explosion. Consult with the gas supply vendor to determine the correct regulators and fittings.
- All gas lines leading from a compressed gas supply should be clearly labeled identifying the gas and the laboratory served.
- Place gas cylinders in such a way that the cylinder valve is accessible at all times. The main cylinder valve should be closed as soon as the gas flow is no longer needed. Do not store gas cylinders with pressure on the regulator. Use the wrenches or other tools provided by the cylinder supplier to open a valve if available. In no case should pliers be used to open a cylinder valve.

Use an approved leak detection liquid to detect leaks (such as *Markal Sure-Chek All Temperature Leak Detector, Nu-Calgon Leak Detector* or *Western Leak Test Solution*). These products can be purchased from the compressed gas cylinder vendor or suppliers such as Grainger. Leak test the regulator, piping system and other couplings after performing maintenance or modifications which could affect the

integrity of the system. <u>Do not use liquid soap</u> or other means for testing for leaks. Soap contains animal fats (lard) and synthetic soap such as dish washing soap (Dawn, Joy, etc.) contains petroleum. These solutions burn easily and may be explosive in an oxygen enriched atmosphere.

- Oil or grease on the high-pressure side of an oxygen cylinder can cause an explosion. Do not lubricate an oxygen regulator or use a fuel/gas regulator on an oxygen cylinder.
- Never bleed a cylinder completely empty. Leave a slight pressure to keep contaminants out (172 kPa or 25 psi). Empty cylinders should not be refilled in the laboratories unless equipped to prevent overfilling.
- Cylinders that held substances with high coefficients of expansion (ammonia) should not be refilled.
- All gas cylinders should be clearly marked with appropriate tags indicating whether they are in use, full, or empty. These disposable tags can be obtained through EH&S.
- Cylinders of toxic, flammable, or reactive gases should be purchased in the smallest quantity possible and stored/used in a fume hood or under local exhaust ventilation. Use the smallest sized returnable cylinder that is available.
- Avoid the purchase of lecture bottles. These cylinders are not returnable, and it is extremely difficult and costly to dispose of them. Your department may be required to pay full cost for disposal of lecture bottles.
- Wear safety goggles, gloves, long sleeved lab coat and closed toe shoes when handling compressed gases that are irritants, corrosive or toxic.
- Flammable gases such as hydrogen or acetylene that are attached to laboratory apparatus such as atomic absorption spectrometers, gas chromatographs, etc. should be equipped with flashback arrestors. Consult with the instrument manufacturer or the gas supply vendor to determine the correct product.
- If you conduct welding operations in your laboratory contact EH&S for information about welding safety and the storage of welding gases.

3.5.2 Special Precautions for Hydrogen

Hydrogen gas has several unique properties that make it a potential danger with which to work. It has an extremely wide flammability range (lower explosive limit, LEL = 4%, upper explosive limit, UEL = 74.5%) making it easier to ignite than most other flammable gases. Unlike most other gases, hydrogen's temperature increases during expansion. If a cylinder valve is opened too quickly the static charge generated by the escaping gas may cause it to ignite. Hydrogen burns with an invisible flame. Caution should therefore be exercised when approaching a suspected hydrogen flame. A piece of paper can be used to tell if the hydrogen is burning. Hydrogen embrittlement can weaken carbon steel, therefore cast iron pipes and fittings must not be used. Seamless tubes should be used. Those precautions associated with other flammable substances also apply to Hydrogen (see Chapter 3.1).

3.5.3 Special Procedures for Toxic Gases

Toxic gases are considered to be those that cause significant acute health effects at low concentrations, have a National Fire Protection Association (NFPA) health rating of 3 or 4, have low occupational exposure limits, or are pyrophoric. Following is a list of gases of special concern and have special requirements. Prior approval from EH&S is required for these toxic gases. Upon approval, an SOP must be written and submitted to EH&S. These gases may not be used in any lab without an EH&S approved SOP.

allene	dichlorosilane	nitric oxide
ammonia	dimethylamine	nitrogen dioxide

arsenic pentafluoride	disilane
arsine	fluorine
boron trichloride	fluorine mixtures
boron trifluoride	germane
bromine pentafluoride	hydrogen bromide
bromine trifluoride	hydrogen chloride
1,3 butadiene	hydrogen cyanide
carbon tetrafluoride	hydrogen fluoride
carbon monoxide	hydrogen selenide
carbonyl sulfide	hydrogen sulfide
chlorine	methyl bromide
chlorine trifluoride	methyl chloride
cyanogens	methyl silane
cyanogens chloride	monomethylamine
diborane	nickel carbonyl

nitrogen trifluoride phosgene phosphine phosphorus pentafluoride phosphorus trichloride phosphorus trifluoride silane silicon tetrafluoride stilbene sulfur tetrafluoride sulfuryl fluoride tungsten hexafluoride vinyl chloride

If these gases are not used and stored in a fume hood they require the use of the following controls:

- Ventilated gas cabinets or enclosures for toxic gas cylinders are mandatory. The exhaust rate of the cabinet must be sufficient to vent a complete cylinder discharge. These units are available commercially and must be obtained by the Principal Investigator.
- Air Flow monitors or alarms on ventilated enclosures or gas cabinets are required.
- Toxic gas alarms for the laboratory are required.
- Gas distribution equipment must use compatible materials and design.
- Critical flow orifices that limit the flow of gas may be needed.
- Documented safety procedures and training of laboratory personnel are required.
- Release scenario modeling including utility and ventilation failure should be prepared.
- Special storage requirements may be required.

3.6 Cryogenic Liquids

<u>Cryogenic fluids</u> are liquid gases at temperatures normally below –238° F. <u>Dewars</u> are specially designed double-walled containers having provisions for pressure relief.

- Cryogenic liquids are extremely cold. Cryogenic liquids and their cold "boil-off" vapor can rapidly
 freeze human tissue and can cause many common materials such as carbon steel, plastics, and rubber
 to become brittle, or even fracture under stress. Liquids in containers and piping at temperatures at
 or below the boiling point of liquefied air (-318° F, 194° C) can actually condense the surrounding air
 to a liquid. Extremely cold liquefied gases (liquid helium and liquid nitrogen) can even solidify air or
 other gases.
- All cryogenic gases also produce large volumes of gas when they vaporize. For example, one volume
 of liquid hydrogen at one atmosphere vaporizes to 700 volumes of hydrogen gas at 70° F and one
 atmosphere of pressure. If these liquids are vaporized in a sealed container, they can produce
 enormous pressures that could rupture the vessel. For this reason, pressurized cryogenic containers
 are usually protected with multiple devices of pressure relief, usually a pressure relief valve for
 primary protection and a frangible disc for secondary protection. Vaporization of liquid oxygen in an
 enclosed area can cause an oxygen-rich atmosphere and could saturate a worker's clothing. Although

oxygen is not flammable it will vigorously support and/or accelerate the combustion of other materials. Vaporization of liquid hydrogen in an enclosed work area can cause a flammable or explosive mixture with air.

• Most cryogenic liquids are odorless, colorless, and tasteless when vaporized to the gaseous state. Most of them have no color as liquids, although liquid oxygen is light blue. However, the extremely cold vapors have a warning property that appears whenever they are exposed to the atmosphere. The cold "boil-off" gases condense the moisture in the air, creating a highly visible fog. The fog normally extends over a larger area than the vaporizing vapor.

3.6.1 Special Handling Procedures

- Liquid nitrogen can cause severe burns. Safety goggles are required during transfer and normal handling of cryogenic materials. If spraying or splashing is possible, then a face shield should be worn for additional protection.
- Dry cryogenic gloves must be worn when handling anything that comes in contact with cold liquids and vapor. Gloves must be loose fitting so they can be removed quickly if liquids are spilled into them. Depending on the application, special clothing may be advisable. It is preferable to wear pants outside of boots or work shoes to deflect any spilled cryogenic material away from your shoes.
- Matches, smoking materials, lighters, and other sources of ignition are prohibited where liquid hydrogen and oxygen are present. All such areas must be designated as "No Smoking".
- Keep dewars vertical at all times. Do not roll the container on its side.
- Make sure the dewar is temperature rated for liquid nitrogen.
- If you use a Thermos bottle with a stainless-steel shell for transporting small amounts of liquid nitrogen do not screw on the cap. If there is inadequate venting the bottle may explode. All containers must have venting lids.
- Do not enter an area where a major spill may have caused an oxygen deficiency. For all major spills, exit the room and call 911. Use liquid nitrogen ONLY in well ventilated areas. Rapid venting can cause near-total displacement of the oxygen in normal air. If the local concentration is 100% nitrogen with no oxygen present asphyxiation is possible. Do not carry liquid nitrogen in a passenger elevator.
- Cryotubes containing samples stored in liquid nitrogen may explode without warning. Tube explosions are thought to be caused by liquid nitrogen entering the tube through minute cracks and then expanding rapidly as the tube thaws. Thaw tubes in a shielded area.
- Evacuated glassware must be shielded against implosion. Exposed glass portions of the container must be taped to minimize flying glass hazards.
- <u>Relief valves on dewars shall not be tampered with under any circumstance.</u>
- Make sure the apparatus in use is correctly pressure rated for the planned application. The pressure rating should be clearly marked. All cryogenic storage vessels must be chosen to withstand the weights and pressures of the material used and must have adequate venting to prevent pressure build-up.
- All cryogenic liquids with boiling points below that of liquid nitrogen, particularly liquid helium and hydrogen, require specially constructed and insulated containers to prevent rapid evaporation.
- Use plastic tweezers to handle superconductors, magnets, or other small cold objects. Test the tweezers for embrittlement before use. Do not touch any object that has been immersed in liquid nitrogen until it warms up to room temperature.
- Many substances become brittle and may shatter when cold. Avoid common glass and large solid plastics.
- Remove metal jewelry/watches on hands and wrists so that it will not freeze and adhere to your skin.
- Filling operations must not be left unattended.

- Make sure the dispensing tube is in good condition and is an approved unit. Check with the gas supply provider for an assessment and equipment selection.
- Transport large dewars in appropriate carts, preferably with brakes.

3.7 Corrosive Chemicals

The major classes of corrosive chemicals are strong acids and bases, dehydrating agents, and oxidizing agents. These chemicals can erode the skin and the respiratory epithelium and are particularly damaging to the eyes. Inhalation of vapors or mists of these substances can cause severe bronchial irritation. If your skin is exposed to a corrosive, flush the exposed area with copious amounts of water for at least fifteen minutes. Then seek medical treatment.

- <u>Strong acids</u> All concentrated acids can damage the skin and eyes and their burns are very painful. Nitric, chromic, and hydrofluoric acids are especially damaging because of the types of burns they inflict. Seek immediate medical treatment if you have been contaminated with these materials (particularly hydrofluoric acid).
- <u>Strong alkalis</u> Common strong bases used in the labs are potassium hydroxide, sodium hydroxide, and ammonia. Burns from these materials are often less painful than acids. However, damage may be more severe than acid burns because the injured person, feeling little pain, often does not take immediate action and the material is allowed to penetrate into the tissue. Ammonia is a severe bronchial irritant and should always be used in a well-ventilated area, such as a fume hood.
- <u>Dehydrating agents</u> This group of chemicals includes concentrated sulfuric acid, sodium hydroxide, phosphorus pentoxide, and calcium oxide. <u>Because much heat is evolved on mixing these</u> <u>substances with water, mixing should always be done by adding the agent to water, and not the</u> <u>reverse, to avoid violent reaction and spattering.</u> Because of their affinity for water, these substances cause severe burns on contact with skin. Affected areas should be washed promptly with large volumes of water.
- Oxidizing agents In addition to their corrosive properties, powerful oxidizing agents such as perchloric and chromic acids (sometimes used as cleaning solutions), present fire and explosion hazards on contact with organic compounds and other oxidizable substances. The hazards associated with the use of perchloric acid are especially severe. It should be handled only after thorough familiarization with recommended operating procedures such as the use of a wash-down hood.

3.7.1 Special Handling Procedures

- Corrosive chemicals should be used in the chemical fume hood, or over plastic trays when handled in bulk quantities (> 1 liter) and when dispensing.
- When working with corrosives wear gloves, goggles, long sleeved lab coat and closed toe shoes. Handling of bulk quantities of these chemicals requires use of rubber aprons and the combined use of face shields and goggles.
- If you are handling bulk quantities on a regular basis an eyewash should be immediately available and a shower close by. Spill materials absorbent pillows, neutral absorbent materials, or neutralizing materials (all commercially available) should be available in the laboratory.
- Store corrosives in cabinets, under the hood or on low shelves, preferably in impervious trays to separate them physically from other groups of chemicals. Keep containers that are not in use in storage areas and off bench tops.
- If it is necessary to move bulk quantities from one laboratory to another or from the stockroom use a safety carrier (rubber bucket with secure lid for secondary containment and protection of the container) or a lab cart.

• At least every three months inspect the shelf clips in your acid cabinet to check for possible corrosion. These shelf clips are the only thing between you and a collapsed shelf. They require special attention.

3.8 Chemicals of High Acute and Chronic Toxicity

Substances that possess the characteristic of high **acute** toxicity can cause damage after a single or short -term exposure. The immediate toxic effects to human health range from irritation to illness and death. Hydrogen cyanide, phosgene, and nitrogen dioxide are examples of substances with high acute toxicity. The lethal oral dose for an average human adult for highly toxic substances ranges from one ounce to a few drops.

Toxicity Rating	Animal LD50 (per kg)		
Extremely toxic (Category 1)	≤5 mg/kg		
Highly toxic (Category 2)	>5 - ≤50 mg/kg		
Moderately toxic (Category 3)	>50 - ≤300 mg/kg		
Slightly toxic (Category 4)	>300 - ≤2,000 mg/kg		
Practically non-toxic	>2,000 mg/kg		

Source: OSHA Regulations, 29 CFR 1910.1200 Appendix A

Oral LD50 data for the rat is listed in the substance's SDS. The LD50 toxicity test is usually the first toxicological test performed and is a good indicator of a substance's acute toxicity. Substances that possess the characteristic of high **chronic** toxicity cause damage after repeated exposure or exposure over long periods of time. Health effects often do not become evident until after a long latency period - twenty to thirty years. Substances that are of high chronic toxicity may be toxic to specific organ systems: they may be described by such terms as hepatotoxins, nephrotoxins, neurotoxins, toxic agents to the hematopoietic system and pulmonary tissue, carcinogens, reproductive toxins, mutagens, teratogens or sensitizers. The definition of each of these categories of toxic substances, and examples of substances that fall into each of these different categories, can be found in Chapter 4 of this manual.

3.8.1 Special Handling Procedures

This Chapter establishes supplemental work procedures to control the handling of substances that are known to exhibit acute or long-term chronic health hazards. The following procedures should be used when the oral LD50 of a substance in the rat is less than 50 milligrams per kilogram body weight for solid materials or nonvolatile liquids and less than 300 mg/kg body weight for volatile liquids or gases.

- Minimize contact with these chemicals by any route of exposure. Protect yourself by wearing gloves, closed toe shoes and long-sleeved laboratory coat. Protect your eyes by safety goggles or glasses. If procedure involving use of these chemicals has a high potential for a splash consider putting on an impermeable apron or coveralls, and possibly a face shield in addition to goggles.
- Use these chemicals in a chemical fume hood or other appropriate containment device if the material is volatile or the procedure may generate aerosols (See guidelines for chemical fume hood use in Chapter 2.3.5). If a chemical fume hood is used it should be evaluated to confirm that it is performing adequately (a face velocity of at least 100 linear feet per minute) with the sash at the operating height.
- Store highly toxic or controlled materials in a locked, dedicated poison cabinet.
- Store volatile chemicals of high acute or chronic toxicity in a ventilated cabinet. Volatile chemicals must be stored in unbreakable primary or secondary containers or placed in chemically resistant trays

(to contain spills). Nonvolatile chemicals should be stored in cabinets or in drawers. Do not store these chemicals on open shelves or counters.

- Decontaminate working surfaces with wet paper towels after completing procedures. Place the towels in plastic bags and secure. Dispose of them in the normal trash if there is only a trace amount on the paper towels. Dispose as hazardous waste if there is a lot of the substance, such as from a spill clean-up. Be sure to label the container with the chemical substance if hazardous waste.
- Volatile chemicals must be transported between laboratories in durable outer containers or on a cart.
- Vacuum pumps used in procedures should be protected from contamination by installing two collection flasks in series along with in-line HEPA-like filter.
- If one or more of these substances are used in large quantities, on a regular basis (three or more separate handling sessions per week), or for long periods of time (4-6 hours) a qualitative, and potentially quantitative, exposure assessment must be performed. In many cases there may be economical commercially available testing strips and meters that can measure the concentration of these materials. The Principal Investigator should contact EH&S if quantitative exposure assessment is required.
- Lab personnel of childbearing age <u>must</u> be informed of any known male and female reproductive toxins used in the lab. It is recognized that exposure to certain chemicals may adversely affect the fertility of the parents or the development of a fetus during pregnancy. Therefore, if you are working with reproductive toxins and are planning to conceive a child or are pregnant, you should consult your medical health care professional regarding risks of exposure and potential exposure control options. Reproductive toxicology information may be found in reference materials on the Internet, by contacting the occupational registered nurse at URI Health Services, and sources such as SDSs.

3.9 Regulated Chemicals and Particularly Hazardous Chemicals

This set of procedures applies to chemical carcinogens listed and regulated by the Occupational Safety and Health Administration (OSHA), and to human carcinogens listed by the International Agency for Research on Cancer (IARC) and the National Toxicology Program (NTP), reproductive toxins, the toxic gases listed in Section 3.4.4, and alkyl methylated mercury compounds such as dimethyl mercury. Please note that a key component of these procedures is the controlled distribution of these substances. Carcinogens are addressed in specific OSHA standards for general industry, shipyard employment, and construction. This link (https://www.osha.gov/SLTC/carcinogens/standards.html) highlights OSHA standards and documents related to carcinogens. OSHA provides information on reproductive hazards (https://www.osha.gov/SLTC/reproductivehazards/hazards.html). Lab users must always refer to the SDS for carcinogen and reproductive hazards, as well as their health care professional.

Note: If you need to purchase dimethyl mercury you must submit a written Standard Operating Procedure to EH&S for approval prior to purchase. One drop on your skin may be lethal.

3.9.1 Special Handling Procedures

- Use these chemicals only in a chemical fume hood or other appropriate containment device (glove box). If a chemical fume hood is used it should be evaluated to confirm that it is performing adequately (a face velocity of at least 100 linear feet per minute (±20%) with the sash at the operating height).
- Volatile chemicals must be stored in a vented storage area in an unbreakable, primary or secondary container or placed in a chemically resistant tray (to contain spills). Nonvolatile chemicals should be stored in cabinets or in drawers. Do not store these chemicals on open shelves or counters. <u>Access to all of these chemicals should be restricted.</u>
- Volatile chemicals must be transported between laboratories in durable outer containers.

- All procedures with these chemicals should be performed in **designated areas**. A chemical fume hood can be considered a designated area or the entire lab could be the designated area. Other employees working in the area should be informed of the particular hazards associated with these substances and the appropriate precautions that are necessary for preventing exposures.
- All designated areas must be posted with a sign that reads:

WARNING

DESIGNATED AREA FOR HANDLING THE FOLLOWING SUBSTANCES WITH HIGH ACUTE OR CHRONIC TOXICITY: [list of substances - identify acute or chronic hazard] [Example: Benzene - carcinogen] AUTHORIZED PERSONNEL ONLY

- Vacuum pumps used in procedures should be protected from contamination by installing two collection flasks in series along with an in-line HEPA -like filter.
- Analytical instruments or other laboratory equipment generating vapors and/or aerosols during their operation, must be locally exhausted or vented in a chemical fume hood.
- Skin surfaces that might be exposed to these substances during routine operations or foreseeable accidents must be covered with appropriate protective clothing. Gloves should be worn whenever transferring or handling these substances. The level of protection should be considered based on a splash risk and may include safety glasses, goggles or a face shield in addition to goggles. Impermeable garments must be used when performing procedures with a high splash potential. When wearing washable garments (such as a laboratory coat), request information from EH&S or your PI/lab supervisor as to the name of URI's dry-cleaning vendor. Do not launder lab coats at home due to the potential for cross contamination. Wear disposable garments if others may be placed at risk during the laundering process. Consider using full body protection (disposable coveralls) if the potential for extensive personal contamination exists.
- All protective equipment must be removed when leaving the designated area and decontaminated (washed) or, if disposable, placed in a plastic bag and secured. If the items are contaminated with very toxic materials dispose of them as hazardous waste. Skin surfaces hands, forearms, face and neck must be washed immediately.
- Work surfaces on which these substances will be handled should be covered with an easily decontaminated surface (such as stainless steel) or protected from contamination with plastic trays or plastic-backed paper. Call EH&S for decontamination and disposal procedures; these will be substance specific. Materials that will be disposed of should be placed in plastic bags and secured.
- Chemical wastes from procedures using these substances must be placed in containers, tagged and disposed of through the hazardous chemical waste program. The wastes must be stored in the SAA in the designated area (defined above) until picked up.
- Normal laboratory work must not be conducted in a designated area until it has been decontaminated or determined to be acceptable by the principal investigator, laboratory supervisor or EH&S.
- If one or more of these substances are used in large quantities, on a regular basis (three or more separate handling sessions per week), or for long periods of time (4-6 hours) a qualitative, and potentially quantitative, exposure assessment should be performed. The principal investigator should consult with EH&S if he/she thinks that a quantitative assessment is needed. In some cases, the principal investigator may need to establish a medical surveillance program if the ambient concentrations exceed the permissible exposure limits.
- Lab personnel of childbearing age must be informed of any known male and female reproductive toxins used in the laboratory. An employee who is pregnant, or planning to become pregnant, and who is working with potential reproductive toxins that might affect the fetus, should consult their

health care professional to evaluate their potential exposure and then take appropriate exposure control measures. Additional guidance can be obtained from the Occupational Health Nurse at URI Health Services.

3.10 Mercury

Elemental mercury has relatively low acute toxicity but does present a potentially significant long-term exposure risk. Mercury can produce colorless, odorless and difficult to detect vapor at room temperature. Large mercury spills are very difficult and expensive to clean-up. The use of mercury should be eliminated wherever possible. Elemental mercury, thermometers, switches and other mercury devices are collected by EH&S as part of the hazardous waste program.

The Environmental Protection Agency (EPA) has identified mercury as a Persistent, Bioaccumulative, and Toxic (PBT) chemical. These materials are highly toxic, long-lasting substances that can build up in the food chain to levels that are harmful to human and ecosystem health. The EPA has targeted these materials for waste minimization.

This link (<u>https://www.epa.gov/toxics-release-inventory-tri-program/persistent-bioaccumulative-toxic-pbt-chemicals-covered-tri</u>) provides a list of chemicals that EPA considers to be the Persistent Bioaccumulative and Toxic Chemicals, the PBTs.

3.10.1 Special Handling Procedures

Replace standard mercury thermometers from incubators, drying ovens, and shakers with spirit-filled thermometers whenever possible. If you cannot find alternatives to mercury in your research, then the following procedures must be followed:

- Remove mercury thermometers from equipment before moving or storing as they are easily broken.
- Containers of mercury must be clearly labeled and sealed at all times. Containers shall only be opened in fume hoods. Shatterproof containers are best and they must be stored within secondary containment bins.
- Do not allow mercury to enter drains or be allowed to evaporate. Protect cup sinks or drains from contamination.
- Portable devices containing mercury, manometers, etc., must be sealed with an airtight and leakproof seal and stored in secondary containment.
- Vacuum pumps must be protected from contamination by liquid mercury and mercury vapor through the use of inline activated carbon filters and/or suitable cold traps.
- Items that have come in contact with mercury or mercury vapor can become contaminated and must be disposed of as hazardous waste or appropriately decontaminated.
- All spills must be cleaned up immediately with a mercury spill kit (contact your lab supervisor or EH&S to obtain a mercury spill kit). Dispose of the clean-up materials as hazardous waste (place in bag, label as mercury waste, and place in SAA). Do not attempt to clean up a spill that is larger than a thermometer. Contact EH&S for assistance.

Chapter 4.0 Introduction to Chemical Toxicology

4.1 Overview

4.1.1 Definitions

Toxicology is the study of the nature and action of poisons.

Toxicity is the ability of a chemical substance or compound to produce injury once it reaches a susceptible site in, or on, the body.

A material's **hazard potential** is the probability that injury will occur after consideration of the conditions under which the substance is used.

4.1.2 Dose-Response Relationships

The potential toxicity (harmful action) inherent in a substance is exhibited only when that substance comes in contact with a living biological system. The potential toxic effect increases as the exposure increases. All chemicals will exhibit a toxic effect given a large enough dose. The toxic potency of a chemical is thus ultimately defined by the dose (the amount) of the chemical that will produce a specific response in a specific biological system.

4.1.3 Routes of Entry into the Body

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

- Absorption through the respiratory tract via inhalation.
- Absorption through the skin or eyes via dermal contact.
- Absorption through the digestive tract via ingestion. (Ingestion can occur through eating or smoking with contaminated hands or in contaminated work areas.)
- Puncture wounds by sharps or needle sticks.

Most exposure standards, such as the Threshold Limit Values (**TLV's**) and Permissible Exposure Limits (**PEL's**), are based on the inhalation route of exposure. These limits are normally expressed in terms of either parts per million (ppm) or milligrams per cubic meter (mg/m³) concentration in air. If a significant route of exposure for a substance is through skin contact, the SDS, PEL and/or TLV will have a "skin" notation. Examples of substances where skin absorption may be a significant factor include pesticides, carbon disulfide, carbon tetrachloride, dioxane, mercury, thallium compounds, xylene and hydrogen cyanide.

4.1.4 Types of Effects

Acute poisoning is characterized by sudden and severe exposure and rapid absorption of the substance. Normally, a single large exposure is involved. Adverse health effects by inhalation are sometimes reversible if the dose is not too large. Examples: 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. Health effects are often irreversible. Examples: lead or mercury poisoning.

A **Local** effect refers to an adverse health effect that 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: strong acids or alkalis.

Systemic effect refers to an adverse health effect that takes place at a location distant from the body's initial point of contact and presupposes absorption has taken place. Examples: arsenic affects the blood, nervous system, liver, kidneys, and skin; benzene affects bone marrow.

Cumulative poisons are characterized by materials that tend to build up in the body as a result of numerous chronic exposures. The effects are not seen until a critical body burden is reached. Example: heavy metals.

Substances in combination: When two or more hazardous materials are present at the same time, the resulting effect can be greater than the effect predicted based on the additive effect of the individual substances. This is called a **synergistic** or **potentiating effect.** Example: exposure to alcohol and chlorinated solvents; or smoking and asbestos.

4.1.5 Other Factors Affecting Toxicity

Rate of entry and **route of exposure**; that is, how fast is the toxic dose delivered and by what means. **Age** can affect the capacity to repair tissue damage.

Previous exposure can lead to tolerance, increased sensitivity or make no difference.

State of health, physical condition and lifestyle 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.

4.1.6 Physical Classifications

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 and be cumulative poisons.

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 airborne concentration. For a proper assessment of the toxic hazard, the size of the aerosol's particles must be determined. A particle's size will determine if a particle will be deposited within the respiratory system and the location of deposition. Particles above 10 micrometers tend to deposit in the nose and other areas of the upper respiratory tract. Below 10 micrometers particles enter and are deposited in the lung. Very small particles (<0.2 micrometers) are generally not deposited but exhaled.

4.1.7 Physiological Classifications

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

Alkaline dusts and mists	Halogens	Ozone
Ammonia	Hydrogen chloride	Phosgene
Arsenic trichloride	Hydrogen fluoride	Phosphorus chlorides
Diethyl/dimethyl sulfate	Nitrogen dioxide	

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

Acetic acid	Formaldehyde	Sulfur dioxide
Acrolein	Iodine	
Formic acid	Sulfuric Acid	

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 overshadowed by a systemic effect resulting from absorption. Examples: hydrogen sulfide, aromatic hydrocarbons.

Asphyxiants have the ability to deprive tissue of oxygen.

Simple asphyxiants are inert gases that displace oxygen. Examples: nitrogen, helium, carbon dioxide, hydrogen.

Chemical asphyxiants reduce the body's ability to absorb, transport, or utilize inhaled oxygen. They are often active at very low concentrations (a few ppm). Examples: carbon monoxide, cyanides.

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

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

Nephrotoxic agents damage the kidneys. Examples: halogenated hydrocarbons, uranium compounds.

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

Carbon disulfide	Tetraethyl lead
Manganese	Thallium
Methyl mercury	Trialkyl tin compounds
Organic phosphorus insecticides	

Some toxic agents act on the **blood** or **hematopoietic system.** The blood cells can be affected directly, or the bone marrow (which produces the blood cells) can be damaged. Examples: aniline, toluidine, nitrobenzene, benzene.

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 silica and asbestos. Other dusts can cause a restrictive disease called **pneumoconiosis.** Examples: Coal dust, Cotton dust, Wood dust.

A <u>carcinogen</u> is an agent that can initiate or increase the proliferation of malignant neoplastic cells or the

development of malignant or potentially malignant tumors. Some known human carcinogens include:

Benzene	Formaldehyde	Chemotherapy drugs
Asbestos	Methylene Chloride	Methyl chloromethyl ether
Alpha-napthylamine	1,2-Dibromo-3-chloropropane (DBCP)	4-nitrobiphenyl
Inorganic arsenic	3,3'-Dichlorobenzidine	N-nitrosodimethylamine
Bis-chloromethyl ether	Ethylene oxide	Vinyl chloride

A <u>mutagen</u> causes heritable changes (mutations) in the genetic material (DNA) of exposed cells. If germ cells are involved, the effect may be inherited and become part of the genetic pool passed onto future generations.

A <u>teratogen</u> (embryotoxic or fetotoxic agent) is an agent which interferes with normal embryonic development without causing a lethal effect to the fetus or damage to the mother. Effects are not inherited. Examples: lead, thalidomide.

A <u>sensitizer</u> is a chemical which can cause an allergic reaction in normal tissue after repeated exposure to the chemical. The reaction may be as mild as a rash (allergic dermatitis) or as serious as anaphylactic shock. Examples: epoxy compounds, toluene diisocyanate, nickel compounds, chromium compounds, poison ivy, chlorinated hydrocarbons.

4.2 Some Target Organ Effects

The following is a categorization of target organ effects that may occur from chemical exposure. Signs and symptoms of these effects and examples of chemicals which have been found to cause such effects are listed.

Toxins	Target organ effect	Signs and symptoms	Example chemicals		
Hepatotoxins	Cause liver damage	Jaundice; liver enlargement	Nitrosamines, chloroform, toluene, perchloro ethylene, cresol, dimethyl sulfate		
Nephrotoxins	Cause kidney damage	Edema; proteinuria	Halogenated hydrocarbons, uranium, chloroform mercury, dimethylsulfate		
Neurotoxins	Nervous system	Narcosis; behavior changes; decreased muscle coordination	Mercury, carbon disulfide, benzene, carbor tetrachloride, lead, mercury, nitrobenzene		
Hematopoietic toxins	Decrease blood function	Cyanosis; loss of consciousness	Carbon monoxide, cyanides, nitro-benzene, aniline, arsenic, benzene, toluene		
Pulmonary toxins	Irritate or damage the lungs	Cough; tightness in chest, shortness of breath	Silica, asbestos, ozone, hydrogen sulfide, chromium, nickel, alcohols		
Reproductive toxins	Reproductive system	Birth defects; sterility	Lead, dibromodichloropropane		
Skin hazards	Dermal layer of the body	Defatting of skin; rashes; irritation	Ketones, chlorinated compounds, alcohols, nickel, phenol, trichloroethylene		
Eye hazards	Affect the eye or vision	Conjunctivitis, corneal damage	Organic solvents, acids, cresol, quinone, hydroquinone, benzol, chloride, butyl alcohol, methanol, bases		

4.3 Occupational Health Standards

Action Level means a concentration designated in 29 CFR 1910 for a specific substance, calculated as an eight (8)-hour time-weighted average which initiates certain required activities such as exposure monitoring and medical surveillance.

TLV: The **threshold limit value** is a recommended occupational exposure guideline published by the American Conference of Governmental Industrial Hygienists. TLV's are expressed as parts of vapor or gas per million parts of air by volume (ppm) or as approximate milligrams of particulate per cubic meter or air (mg/M3). The TLV is the average concentration of a chemical that most people can be exposed to for a working lifetime with no ill effects. The TLV is an advisory guideline. If applicable, a **ceiling concentration (C)** that should not be exceeded or a **skin** absorption notation (S) will be indicated with the TLV.

PEL: The **permissible exposure limit** is a legal standard issued by OSHA. Unless specified, the PEL is a time weighted average **(TWA)**.

TWA: Most exposure standards are based on **time weighted averages**. The TWA is the average exposure over an eight (8) hour workday. Some substances have Ceiling (C) limits. Ceiling limits are concentrations that should never be exceeded.

The SDS will list the occupational health standard(s) for the hazardous chemical or each component of a mixture.

The NIOSH Guide provides a complete listing of these values. A copy is available at EH&S or it may be viewed on the Internet at NIOSH Pocket Guide to Chemical Hazards: <u>http://www.cdc.gov/niosh/npg/npg.html</u>

Appendix I List of Compressed Gases with NFPA Rating 3 or 4 or Pyrophoric

	NFPA Health		Corrosive or	Toxic (LC50>200 ppm but <2000	Highly Toxic
Dangerous Gas (CAS#)	Hazard	Exposure Limits	Pyrophoric	ppm but <2000 ppm)	(LC50<200 ppm)
Allene (463-49-0)	3	Exposure Linits	Fyrophone	ppin)	(LC30<200 ppin)
Ammonia (7664-41-7)	3	35 ppm (STEL)	CORROSIVE		
Arsenic pentafluoride (7784-36-3)	4	5 mg/m3 (IDLH)	CORROSIVE		
Arsine (7784-42-1)	4	3 ppm (IDLH)	CONTOSIVE		120 ppm
Boron trichloride (10294-34-5)	3	100 ppm (IDLH)	CORROSIVE		120 ppm
Boron trifluroide (7637-07-2)	3	3 ppm (C)	CORROSIVE	417 ppm	
Bromine pentafluoride (7789-30-2)	3	0.1 ppm PEL	CORROSIVE	117 ppm	50 ppm
Bromine trifluoride (7787-71-5)	4	5 ppm (STEL)	CORROSIVE		50 ppm
1,3-butadiene (106-99-0)	4	10 ppm (STEL)	CONTROSIVE		30 ppm
Carbon tetrafluoride (75-73-0)	3	10 pp (0122)			
Carbon monoxide (630-08-0)	2	35 ppm (PEL)			
Carbonyl fluoride (75-73-0)	3	5 ppm (STEL)		360 ppm	
Carbonyl sulfide (463-58-1)	3	o pp (0.11)	CORROSIVE	1070 ppm	
Chlorine (7782-50-5)	3	1 ppm (STEL)	CORROSIVE	293 ppm	
Chlorine trifluoride (7790-91-2)	4	0.1 ppm (C)	CORROSIVE	229 ppm	
Cyanogens (460-19-5)	4	10 ppm (PEL)	CORROSIVE	350 ppm	
Cyanogen chloride (506-77-4)	4	0.3 ppm (C)	CONTROSIVE	550 ppm	
Diborane (19278-45-7)	4	0.1 ppm (PEL)	PYROPHORIC		80 ppm
Dichlorosilane (4109-96-0)	3	0.2 pp (. 22)	CORROSIVE	215 ppm	
Dimethylamine (124-40-3)	3	5 ppm (PEL)	0011100112	220 pp	
Fluorine (7782-41-4)	4	25 ppm (IDLH)	CORROSIVE		185 ppm
Germanium tetrahydride (germane) (7782-65-2)	4	0.2 ppm (PEL)		442 ppm	
Hydrogen bromide (10035-10-6)	3	30 ppm (IDLH)		· ·= pp	
Hydrogen chloride (7647-01-0)	3	50 ppm (IDLH)	CORROSIVE		
Hydrogen cyanide (74-90-8)	4	50 ppm (IDLH)			160 ppm
Hydrogen fluoride (7664-39-3)	3	30 ppm (IDLH)	CORROSIVE	1276 ppm	
Hydrogen selenide (7783-07-5)	3	1 ppm (IDLH)			
Hydrogen sulfide (7783-06-4)	3	100 ppm (IDLH)		444 ppm	
Methyl bromide (74-83-9)	3	250 ppm (IDLH)	CORROSIVE	302 ppm	
Methyl chloride (74-87-3)	2				
Methylsilane (992-94-9)	3				
Monomethylamine (74-89-5)	3			448 ppm	
Nickel carbonyl (13463-39-3)	4				35 ppm
Nitric oxide (10102-43-9)	3	100 ppm (IDLH)			131 ppm
Nitrogen dioxide (10102-44-0)	4	1 ppm (C)	CORROSIVE		117 ppm
Nitrogen trifluoride (7783-54-2)	3	5 ppm (C)	CORROSIVE	2000 ppm	
Phosgene (75-44-5)	4	2 ppm (IDLH)			50 ppm
Phosphine (7803-51-2)	4	50 ppm (IDLH)	PYROPHORIC		11 ppm
Phosphorous pentafluoride (7647-19-0)	3		CORROSIVE		
Phosphorous trichloride (7719-12-2)	3	0.5 ppm (STEL)	CORROSIVE		104 ppm
Phosphorous trifluoride (7783-55-3)	3				
Silicon tetrahydride (silane) (7803-62-5)	2		PYROPHORIC		
Silicon tetrafluoride (7783-61-1)	3				
Stibine (7803-52-3)	4	5 ppm (IDLH)			100 ppm
Sulfur tetrafluoride (7783-60-0)	4		CORROSIVE		19 ppm
Sulfuryl fluoride (2699-79-8)	3	200 ppm (IDLH)		991 ppm	
Tungsten hexafluoride (7783-82-6)	3	3 mg/m3 (STEL)	CORROSIVE		118 ppm
Vinyl chloride (75-01-4)	4	5 ppm (C)		390 ppm	