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Chemical Hygiene Plan

Providence College

Office of Environmental, Health & Safety

Preface

The Providence College Chemical Hygiene Plan has been prepared in compliance with the requirements of the Occupational Safety and Health Administration (OSHA) Standard 29 CFR 1910.1450: Occupational *Exposure to Hazardous Chemicals in Laboratories*. It establishes policies and procedures to protect members of the Providence College Community from the hazards of laboratory use of hazardous chemicals. While the OSHA Standard applies only to employees of the College, the same standards of protection are established for students and other members of the Community.

The Chemical Hygiene Program established by this Plan is administered by the Providence College Office of Environmental Health and Safety with the technical assistance of the Chemical Hygiene Officer. Questions regarding the Program should be addressed to the Office of Environmental Health and Safety.

This Plan applies only to the "laboratory use" of chemicals as defined by OSHA. Chemical use elsewhere on campus is covered by the Providence College OSHA Hazard Communication Standard Program in compliance with 29 CFR 1910.1200. Similarly, separate policies and procedures have been established for protection from other laboratory hazards. For example, radiation hazards are controlled by the radiation protection procedures.

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Section 1: Standard Safety Procedures

Chapter 1: Program Objectives and Responsibilities

A. Chemical Hygiene Program Objectives

The objectives of the Providence College Chemical Hygiene Program are twofold.

- 1. To provide a safe environment for faculty, staff, students, and visitors in the laboratories of Providence College.
- 2. To comply with the OSHA Laboratory Standard¹ and other applicable federal, state, and local regulations regarding chemical safety.

This Chemical Hygiene Plan describes policies and procedures designed to achieve those objectives. It identifies the minimum requirements for working in College laboratories. Departments and individual faculty members may establish additional safety requirements to address hazards specific to their operations and to ensure the health and safety of the students, staff, and visitors under their supervision.

B. Activities Covered by the Chemical Hygiene Plan

This Plan applies to those activities regulated by the OSHA Laboratory Standard that covers the laboratory use of hazardous chemicals, with "laboratory," "laboratory use," and "laboratory scale" defined as follows.

"Laboratory" is defined as a facility where the laboratory use of hazardous chemicals occurs. It is a workplace where relatively small quantities of chemicals are used on a non-production basis.

"Laboratory use of hazardous chemicals" is defined as handling or use of such chemicals in which all the following conditions are met:

- (i) Chemical manipulations are carried out on a "laboratory scale";
- (ii) Multiple chemical procedures or chemicals are used;
- (iii) The procedures involved are not part of a production process, nor in any way simulate a production process; and
- (iv) Protective laboratory practices and "equipment" are available and in common use to minimize the potential for employee exposure to hazardous chemicals.

¹OSHA Standard 29 CFR 1910.1450 "*Occupational Exposure to Hazardous Chemicals in Laboratories*" is referred to as the OSHA Laboratory Standard throughout this Plan.

"Laboratory scale" is defined as work with substances in which the containers used for reactions, transfers, and other handling of substances are designed to be easily and safely manipulated by one person.

This Plan applies to all laboratories, as defined by OSHA above, in the Departments of Biology, Chemistry and Biochemistry, Psychology, and Engineering Physics Systems.

C. Responsibilities of the Chemical Hygiene Officer

The Chemical Hygiene Officer shall:

- 1. Determine which activities fit the OSHA definition of "laboratory use of hazardous chemicals";
- 2. Develop policies and procedures necessary to achieve the safety objectives stated above as presented in this Chemical Hygiene Plan;
- 3. Conduct periodic laboratory compliance reviews and recommend corrective actions as necessary;
- 4. Provide or coordinate laboratory safety training for all laboratory employees (faculty, staff, and student employees) and support staff (e.g. custodians);
- 5. Assist faculty members in establishing safety procedures for individual laboratories;
- 6. Provide technical services, such as exposure monitoring; and
- 7. Review this Plan annually and update it as necessary.

Additional duties with regard to implementation of this Chemical Hygiene Plan are described throughout this document.

D. Responsibilities of Faculty and Teaching Staff

The faculty and teaching staff are responsible for:

- 1. Following the policies and procedures of this Chemical Hygiene Plan in their laboratories;
- Conducting a risk assessment prior to beginning any work with any hazardous substance. The faculty member conducting the assessment should determine the appropriate protective measures to be used including containment, engineering controls, personal protective equipment, and safe lab procedures. One reference for conducting this risk assessment is the ACS Guide, <u>Identifying and Evaluating Hazards in Research Laboratories</u>, which can be found at <u>https://goo.gl/fcslO7</u>;
- 3. Acquiring information needed to recognize and control hazards in the laboratory;
- 4. Identifying laboratory practices that reduce the risk of injury or chemical exposure;
- 5. Informing anyone working under their supervision of the specific hazards associated with hazardous substances via relevant Chemical SOPs and the required safety procedures associated with working in their lab(s) via relevant Laboratory SOP(s). This training is to be conducted and documented prior to any work in the laboratory and at least annually thereafter;
- 6. Arranging for immediate response to injuries or other emergencies in areas under their supervision;
- 7. Reporting any unsafe conditions which cannot be immediately remedied;

- 8. Completing laboratory safety training before beginning work in the lab, and at least annually thereafter;
- Informing employees under their supervision who use hazardous substances or frequent areas where hazardous substances are used that they must complete laboratory safety training;
- 10. Providing required information to all lab workers under their supervision who are working with formaldehyde as described in Chapter 13;
- 11. Establishing guidelines for their laboratory which describe what laboratory procedures require their prior approval;
- 12. Conducting annual safety inspections or ensuring that responsible laboratory personnel conduct safety inspections of laboratories under their supervision, and correcting any safety issues revealed during such inspections in a timely manner;
- 13. Completing accident reports for all laboratory accidents. Reports are to be submitted to the Department Chair, who will forward a copy to the Office of Environmental Health and Safety ("EHS Office");
- 14. Providing health and safety information requested by the EHS Office.

E. Responsibilities of Staff and Student Employees

All staff members and student employees are responsible for:

- 1. Knowing and complying with the policies and procedures of this Chemical Hygiene Plan and other health and safety policies or procedures established by the Department or supervising faculty member;
- 2. Reporting all accidents, chemical spills, and unsafe conditions to the supervising faculty member; and
- 3. Completing health and safety training at the request of the supervising faculty member.

F. Responsibilities of Students

All students are responsible for:

- 1. Working in a safe and responsible manner in the laboratory;
- 2. Performing all work in accordance with the procedures established by the Department and supervising faculty member;
- 3. Wearing required personal protective equipment;
- 4. Following established emergency procedures in the event of an accident or chemical spill; and
- 5. Reporting all accidents, chemical spills, and unsafe conditions to the supervising faculty member.

G. Disciplinary Action

Failure to follow safety rules and regulations is a violation of College policy and major offenses will be reported to the Department Chair and/or Dean of Arts & Sciences. If an issue of concern is noted, the laboratory will be re-inspected after a determined period of time to verify that adjustments have been made. If the same problem persists, the Chemical Hygiene Officer will send a report to the Dean of Arts & Sciences, and if necessary, to the Assistant Vice President for Environmental Compliance.

H. Availability of the Chemical Hygiene Plan

Faculty and full time staff members are provided with a copy of this Chemical Hygiene Plan for their use and the use of employees and students under their supervision. Additional copies can be obtained from the EHS Office. It is also available online.

Chapter 2: General Rules

A. Controlling Sources of Exposure

All experiments must be designed and carried out to minimize exposure to hazardous substances. Source reduction, engineering controls, and protective equipment, in that order, are the three primary means of controlling exposure. The following are examples of source reduction and engineering control techniques.

Source Reduction

- Use the smallest amount of a hazardous substance that will serve the intended purpose.
- Design experiments to use the minimum amount of a hazardous substance required.
- Always close containers when not in use.
- Minimize the surface area of open containers (e.g. use of an Erlenmeyer flask instead of a beaker).

Engineering Controls

- Use fume hoods whenever possible.
- Avoid the use of fume hoods for long-term storage of equipment or hazardous chemicals (see Chapter 3).
- Avoid the release of hazardous substances in cold rooms as they have re-circulating air systems.
- Use equipment and glassware only for its designed purpose. Never use damaged equipment or glassware.
- If operations must be left unattended, provide for containment of hazardous substances in the event of equipment failure.

Protective Equipment

While minimum levels of protective equipment are required as described in Chapter 4, it should be recognized that source reduction and engineering controls are generally more effective means of exposure control.

B. Personal Hygiene

Good personal hygiene practices are essential to minimize exposure to hazardous substances and potential injury from other hazardous conditions in the laboratory such as broken glass.

• The storage or consumption of food or beverages, application of make-up, and smoking are prohibited in all laboratories and chemical storage areas.

- Avoid "routine" exposures. Do not smell, taste, or mouth pipette any substances.
- Always wash hands immediately upon contamination, after handling hazardous chemicals, and before leaving the laboratory.
- Long hair and loose clothing must be confined.
- Wash contaminated clothing or lab coats separately from other clothing.

C. Housekeeping

Keeping the laboratory work area organized and clean is essential to safe handling of hazardous materials. Only the equipment and chemicals necessary for the particular procedure being performed should be kept in the work area. This is particularly important when working in a fume hood as storage of numerous containers or pieces of equipment can severely diminish the effectiveness of the hood. If several people are working in the same laboratory, requirements for space and hood access should be discussed and work areas agreed upon.

Floors and surfaces should be kept clean and spills cleaned up immediately as described in Chapter 14. The entire work area should be cleaned-up at the end of each day.

D. Safety Data Sheets

Chemical manufacturers, distributors, and importers are responsible for providing Safety Data Sheets (SDSs) to communicate the hazards of hazardous chemical products. These sheets are either supplied with the products when shipped or available electronically. SDSs should be stored in or electronically accessible from the laboratories in which the substances are used.

E. Unattended Operations

Avoid leaving operations unattended. When it is necessary to leave an experiment involving hazardous substances unattended, provide for containment in the event of equipment failure. Additionally, leave the lights on and place a warning sign on the door if, in the event of an emergency, there would exist a hazard to persons entering the room. Leave an emergency contact number on the sign.

F. Reporting of Unsafe Conditions

It is the responsibility of each individual to be alert to unsafe conditions in the laboratory, and to take necessary actions to prevent injury (e.g., turning off faulty equipment, posting signs). All unsafe conditions which cannot be immediately remedied should be reported to the responsible faculty member, who should contact the Chemical Hygiene Officer if necessary.

G. Music

No earbuds/headphones are permitted in teaching or research labs.

H. Open Flames

Open flames should not be used near combustible materials. This not only includes flammable chemicals, but also combustible items such as loose papers and signs.

I. Vacuum Lines

Any connection to a vacuum line, via an aspirator bottle, suction flask, or any other apparatus, should be connected to an overflow collection flask. Depending on the usage, an inline HEPA filter may be necessary to protect the house vacuum and vacuum pumps. Any apparatus connected to the vacuum line should have proper hazard labeling unless the setup is removed by the end of the work day. An appropriate disinfectant should be used when biological agents are involved. See the College's Biosafety Manual for full details.

J. Animal Care & Use Program

All work with animals covered under an IACUC protocol must comply with the College's Animal Occupational Health and Safety Program Policy.

K. Biosafety Program

All work with biological agents must comply with the College's Biosafety Manual.

Chapter 3: Ventilation Equipment

A. Fume Hoods

The EHS Office checks fume hood performance annually. Acceptable performance is defined as an average face velocity of 100-150 linear feet per minute (Ifm) with the sash open to 15 inches from the hood floor. Face velocities of 80-100 Ifm are marginal, and those under 80 Ifm are unacceptable. Hoods with unacceptable performance are posted with "Do Not Use" signs until repaired.

Noise level or indicator lights should not be relied upon to ensure that a hood is functioning. An airflow check can be conducted by the instructor prior to hood operation by holding a Kimwipe at the hood opening to determine if there is inward air flow. If there is no inward flow, post a "Do Not Use" sign on the hood and contact the Physical Plant and EHS Office.

The fume hood's effectiveness depends on laminar air flow passing through the face of the hood and through the baffles in the back of the hood. This air flow is very sensitive to the movement of air in the room and the set-up inside the hood. The following guidelines should be observed:

- 1. Keep the hood as uncluttered as possible.
- 2. Do not walk rapidly by the face of the hood.
- 3. The first 6" of the fume hood surface should be kept clear of solutions and equipment, in order to maintain easy access to the interior of the hood, and prevent items from being accidentally knocked to the floor when removing arms and hands from the hood.
- 4. All laboratories are under negative pressure when the hoods are on to prevent contaminated air from entering the corridors. Therefore, hoods should be on whenever hazardous substances are being used in a laboratory to ensure that negative pressure is maintained and exhaust from the laboratory is maximized.

B. Biosafety Cabinets

Biosafety cabinets serve as the primary barrier to protect workers and the environment from exposure to infectious biological aerosols generated during the manipulation of infectious agents.

The EHS Office coordinates annual testing of biosafety cabinets to certify that NSF-49 specifications are met. A certification sticker should be posted on each biosafety cabinet.

The "air curtain" along the face of the cabinet is very sensitive to the movement of air in the room. The following guidelines should be observed:

1. Do not block vent along front ridge.

- 2. Do not move your arms rapidly through the face of the cabinet.
- 3. Do not walk rapidly by the face of the cabinet.
- 4. Keep the cabinet as uncluttered as possible.
- 5. The UV light should be turned off when the room is occupied to protect the eyes and skin from ultraviolet light, which can burn the cornea and cause skin cancer.
- 6. In general, work flow should be set up from one end of the cabinet to the other, with one "clean" end and one "contaminated" end.

For full rules and guidelines for working with infectious agents in biosafety cabinets, see the College's Biosafety Manual.

C. Glove Boxes

Glove boxes can be used when it is necessary to operate under inert atmosphere. Inspect gloves before use and replace gloves showing any sign of damage or other deterioration.

Chapter 4: Protective Clothing and Equipment

Protective clothing and equipment must be worn to guard against injuries. Each faculty or supervising staff member is responsible for conducting a risk assessment before working with a new hazardous chemical; performing a new procedure; and for choosing protective equipment appropriate for the materials, experimental procedures, and amounts handled. SOPs, if required for the substances handled, should document the results of the hazard assessment and explain the selection of appropriate protective equipment.

A. Skin Coverage

Proper clothing must be worn when working with hazardous materials in the laboratory. No skin should be exposed below the waist. Short dresses, skirts, shorts, tank tops, loose fitting clothing, or clothing that leaves the mid-section and chest area exposed may not be worn in the laboratory unless lab coats or other protective clothing is also worn. Long hair should be tied back and shoes must cover the entire foot. For highly hazardous operations, the faculty member in charge will determine which materials and processes require clothing that fully covers the upper body.

B. Eye Protection

Eye protection is required when using hazardous substances in the lab. Chemical splash goggles provide protection from splashing chemicals or flying particles. Safety glasses with side shields provide some protection from flying particles but only minimal protection against splashing chemicals. Safety glasses instead of goggles may only be worn at the discretion of the supervising faculty member, who should have sufficient knowledge of the chemicals and the operation to determine if safety glasses offer enough protection. The supervising faculty member shall notify the Chemical Hygiene Officer of any operation that he/she decides to use safety glasses instead of goggles.

Teaching assistants and visitors must follow the same eye protection requirements as outlined above. In the case of shared research labs, the faculty should discuss appropriate eye protection to protect against all laboratory hazards.

Eye protection should be stored in such a way as to prevent chemical contamination, dust, and scratches.

The use of UV and/or IR protective safety glasses is required when working with instruments generating and releasing UV or IR emissions unless a safety mechanism automatically shuts off the emission source when exposure is possible.

A selection tool has been published online (<u>https://goo.gl/wRe38F</u>), based on the ANSI eye protection standard, Z87.1-2015, that shows various kinds of safety glasses and the hazards against which they protect. All protective eyewear worn in the laboratory must meet the ANSI Z87.1 standard.

C. Gloves

Decisions regarding the need to wear gloves are dependent on the hazard(s) of the substance and the potential for contamination during the experiment. These decisions are made by laboratory supervisors.

Proper glove selection should be based on the chemical resistance of the glove material and dexterity requirements. A glove material's chemical resistance is a function of the permeation rate and breakthrough time. There is no one glove that protects against all chemicals. The recommendations of the glove manufacturer and the Safety Data Sheet for the particular chemical should be consulted when choosing appropriate gloves. Most glove manufacturers publish glove selection guides online that indicate glove compatibility for a variety of different chemicals.

D. Clothing

The purpose of protective clothing is to prevent contamination of the skin and to prevent the carrying of contaminants outside the laboratory. Street clothes may afford limited skin protection and if worn while handling hazardous chemicals, may result in contaminants being carried outside the laboratory. Laboratory coats or aprons or aprons with disposable sleeve protectors must be worn when handling:

- any quantity of an Acute Toxin (see Chapter 22)
- any quantity of Select Carcinogens (see Chapter 22), Reproductive Toxins (see Chapter 22), which is readily absorbed through the skin (see Table 4.1),
- greater than one liter or 500 grams of any other Select Carcinogen or Reproductive Toxin,
- greater than one liter of concentrated (as supplied by the manufacturer) acids and bases.²

When working with pyrophorics and explosives, NOMEX 3A flame-resistant lab coats must be worn. Flame resistant lab coats (NOMEX or FR-treated cotton) should be worn when working with >1L of category 1 or 2 flammable liquids (flash point < $73^{\circ}F$ / GHS hazard rating of H224

 $^{^{2}}$ Lab coat requirements do not apply to the use of stationary containers equipped with pumps when less than one liter is being dispensed.

or H225). In addition, non-synthetic clothing (including long pants and shoes that cover the entire foot) should be worn, and no skin should be exposed below the waist.

Specialized protective clothing is necessary in certain high hazard operations (e.g., hydrofluoric acid as described in Chapter 21).

E. Respiratory Protection

Respiratory protection is generally not required in the laboratory. Hazardous substances should be handled in the fume hoods whenever feasible. Should respiratory protection be required, the EHS Office will evaluate the operation.

Faculty members who wish to use a dust mask or other respirator voluntarily – not for personal protection – may request one from the EHS Office. Under OSHA Regulation, the EHS Office must determine if such respirator use will in itself create a hazard. If not, respirator use will be granted. In such cases, the supervising faculty member and those working under his/her direction will be issued a copy of OSHA's "Appendix D," which advises users of the limitations of respirator use.

F. Protective Equipment Hygiene

When using personal protective equipment, care should always be taken to keep contaminants within the laboratory. Contaminated gloves and clothing should be disposed of immediately in the proper waste receptacle. Gloves and lab coats should not be worn outside the laboratory, with the following exceptions:

- When transporting hazardous chemicals through hallways, wear one glove, leaving the other hand free to open doors, press elevator buttons, etc.
- A lab coat is permitted for movement directly between labs, as long as the lab coat is free of overt contamination.

DIEPOXYBUTANE

DIETHYL SULPHATE

DIEPOXYBUTANE, 1,2:3,4-

DIEPOXYBUTANE, 3,4-, MESO 1,2

Table 4.1: "Particularly Hazardous Substances" that are skin-absorbed			
Name	CAS #	Hazard	
2,4,5-T	000093-76-5	RT	
ACROLEIN	000107-02-8	SC	
ACRYLAMIDE	000079-06-1	SC	
ACRYLONITRILE	000107-13-1	AT,SC,RT	
AMINODIPHENYL,4-	000092-67-1	SC,RT	
AMMONIUM DICHROMATE (VI)	007789-09-5	SC	
ANILINE AND COMPOUNDS	000062-53-3	AT	
ANISIDINE, ORTHO-	000090-04-0	SC	
ARSENEOUS ACID, CALCIUM SALT	027152-57-4	SC,RT	
AZIRIDINE	000151-56-4	SC	
BENZ[a]ANTHRACENE	000056-55-3	SC	
BENZENE	000071-43-2	SC,RT	
BENZIDINE	000092-87-5	SC	
BENZIDINE-BASED DYES	000000-00-0	SC	
BENZYLTRICHLORIDE	000098-07-7	SC	
CADMIUM CHLORIDE	010108-64-2	SC,RT	
CARBON DISULFIDE	000075-15-0	RT	
CARBON TETRACHLORIDE	000056-23-5	SC	
CATECHOL	000120-80-9	SC	
CHLORDANE AND ISOMERS	000057-74-9	SC,RT	
CHLOROMETHYL ETHER,BIS-	000542-88-1	SC,RT	
CHLOROANILINE, PARA	000106-47-8Z	SC	
CHLOROPHENOLS	000095-57-8	SC	
CHLOROPHENOXY HERBICIDES	000000-00-0	SC	
CHLOROPRENE	000126-99-8	SC,RT	
CHROMIC ACID, DISODIUM SALT	007775-11-3	SC	
COAL-TAR AND DISTILLATE, DYE, PITCHES	008007-45-2	SC	
CYANAMIDE	000420-04-2	AT	
CYANIDE AND COMPOUNDS	000057-12-5	AT	
DDT	000050-29-3	SC,RT	
DECABORANE	017702-41-9	AT	
DIAZEPAM	000439-14-5	RT	
DIBROMO-3-CHLOROPROPANE,1,2-	000096-12-8	SC,RT	
DICHLORO-2,2-BIS(P-CHLOROPHENYL)ETHANE, 1,1- (DDD)	000072-54-8	SC	
DICHLOROBENZIDINE, DIHYDROCHLORIDE, 3,3' -	000612-83-9	SC	
DICHLOROBENZIDINE,3,3'-	000091-94-1	SC	
DICHLOROETHANE, 1,2-	000107-06-2	SC,RT	
DICHLOROPROPENE, 1,3- (TECHNICAL-GRADE)	000542-75-6	SC	
DICHLORVOS	000062-73-7	AT,SC,RT	

1. 4 7 " ...

001464-53-5

000298-18-0

000564-00-1

000064-67-5

SC,RT

SC,RT

SC,RT

SC

DIETHYLSTILBOESTROL	000056-53-1	SC,RT
DIMETHYL MERCURY	000593-74-8	AT,RT
DIMETHYL SULFATE	000077-78-1	AT,SC,RT
DIMETHYL SULFOXIDE	000067-68-5	RT
DIMETHYLBENZIDINE, 3,3'- (0-TOLIDINE)	000119-93-7	SC
DIMETHYLFORMAMIDE	000068-12-2	SC,RT
DIMETHYLHYDRAZINE, 1,1-	000057-14-7	SC,RT
DIMETHYLHYDRAZINE, 1,2-	000540-73-8	SC,RT
DINITROTOLUENE, 2,4-	000121-14-2	SC
DIOXANE, 1,4-	000123-91-1	SC
ENDOSULFAN	000115-29-7	AT,RT
ENDRIN	000072-20-8	AT
EPICHLOROHYDRIN	000106-89-8	SC,RT
ETHYL ACRYLATE	000140-88-5	SC
ETHYLENE CHLOROHYDRIN	000107-07-3	AT
ETHYLENE DIBROMIDE	000106-93-4	SC
FORMALDEHYDE	000050-00-0	SC,RT
FURAN	000110-00-9	SC
GASOLINE	008006-61-9	SC
GLYCIDALDEHYDE	000765-34-4	SC
GLYCIDOL	000556-52-5	SC,RT
HEPTACHLOR	000076-44-8	AT,SC,RT
HEPTACHLOR EPOXIDE	001024-57-3	AT,SC,RT
HEXACHLOROBENZENE	000118-74-1	SC,RT
HEXACHLOROBENZENE, GAMMA	000058-89-9	SC,RT
HEXACHLOROCYCLOHEXANES	000000-00-0	SC
HEXACHLOROHEXANES	000608-73-1	SC
HEXAMETHYLPHOSPHORAMIDE	000680-31-9	SC,RT
HYDRAZINE	000302-01-2	SC,RT
HYDRAZINE, SULFATE	010034-93-2	SC,RT
HYDROGEN CYANIDE	000074-90-8	AT
HYDROGEN FLUORIDE	007664-39-3	AT
HYDROGEN SELENIDE	007783-07-5	AT
KEPONE (CHLORDECONE)	000143-50-0	SC,RT
MANGANESE TRICARBONYL METHYLCYCLOPENTADIENYL	012108-13-3	AT
MECOPROP	000093-65-2	SC
MERCURY AND COMPOUNDS	007439-97-6	RT
METHYL BROMIDE	000074-83-9	AT,RT
METHYL HYDRAZINE	000060-34-4	AT,RT
METHYL ISOCYANATE	000624-83-9	AT
METHYL MERCURY AND COMPOUNDS "s"	022967-92-6	AT,SC,RT
METHYLAZIRIDINE, 2-	000075-55-8	AT,SC,RT
METHYLENE BIS(2-CHLOROANILINE), 4,4- (MBOAC)	000101-14-4	SC
MINERAL OILS, UNTREATED AND MILDLY TREATED	000000-00-0	SC
MIREX	002385-85-5	SC,RT

MUSTARD GAS (SULPHUR MUSTARD)	000505-60-2	AT,SC,RT
NAPHTHYLAMINE, 2-	000091-59-8	SC,SC
NAPHTHYLAMINE, ALPHA-	000134-32-7	
NICOTINE	000054-11-5	AT,RT
NITRIC ACID (FUMING)	007697-37-2	AT
NITROBENZENE	000098-95-3	SC
NITROFEN (TECHNICAL-GRADE)	001836-75-5	SC
NITROGEN MUSTARD	000051-75-2	AT,SC,RT
NITROGEN MUSTARD HYDROCHLORIDE	000055-86-7	AT,SC,RT
NITROGEN MUSTARD N-OXIDE	000126-85-2	AT,SC,RT
NITROGEN MUSTARD N-OXIDE HYDROCHLORIDE	000302-70-5	AT,SC,RT
PARATHION	000056-38-2	AT,RT
PCB (AROCLOR 1254)	011097-69-1	SC,RT
PCB (AROCLOR 1260)	011096-82-5	SC,RT
PENTACHLOROPHENOL	000087-86-5	AT,SC
PHENYL GLYCIDYL ETHER	000122-60-1	SC
PROPANE SULTONE, 1,3-	001120-71-4	SC,RT
PROPIONIC NITRILE	000107-12-0	AT
PROPYLENE OXIDE	000075-56-9	AT,SC,RT
SHALE-OILS	068308-34-9	SC
SODIUM AZIDE	026628-22-8	AT,RT
SODIUM DICHROMATE (VI)	010588-01-9	SC,RT
SODIUM FLUOROACETATE	000062-74-8	AT
STYRENE	000100-42-5	SC,RT
STYRENE-7,8-OXIDE	000096-09-3	SC,RT
SULFALLATE	000095-06-7	SC
SULFURIC ACID, DIISOPROPYL ESTER	002973-10-6	SC
TETRACHLORODIBENZO-para-DIOXIN, 2,3,7,8- (TCCD)	001746-01-6	AT,SC,RT
TETRACHLOROETHYLENE	000127-18-4	SC,RT
TETRAETHYL LEAD	000078-00-2	AT,SC,RT
TETRAETHYL PYROPHOSPHATE	000107-49-3	AT
TETRAMETHYL SUCCINONITRILE	003333-52-6	AT
THALIDOMIDE	000050-35-1	RT
THIOPHENOL	000108-98-5	AT
TOLUENE	000108-88-3	RT
TOLUIDINE, ORTHO-	000095-53-4	AT,SC
TOXAPHENE (POLYCHLORINATED CAMPHENES)	008001-35-2	SC,RT
TRICHLOROPHENOL, 2,4,6-	000088-06-2	SC
TRICHLOROPROPANE, 1,2,3-	000096-18-4	SC
TRIS-1,2,3-DIBROMOPROPYL PHOSPHATE	000126-72-7	SC
VINYL-1-CYCLOHEXENE DIEPOXIDE, 4-	000106-87-6	SC
WARAFIN	000081-81-2	RT
XYLIDINE	001300-73-8	AT,SC

AT - acute toxin

SC - select carcinogen

4: Protective Clothing and Equipment

RT - reproductive toxin

Chapter 5: Emergency Equipment

A. Fire Extinguishers

Each faculty member should review the hazards in his/her laboratory on an ongoing basis to determine if the fire extinguisher(s) present are appropriate. If additional or different class extinguishers are needed, the faculty member should notify the Chemical Hygiene Officer who will in turn notify Physical Plant.

Table 5.1: Classes of Fire Extinguishers

Class	Type of fire extinguisher is good for
Class A	Wood, cloth, paper, rubber, plastics
Class B	Flammable liquids, oils, greases, tars, oil-based paints, and flammable gases
Class C	Energized electrical equipment
Class D	Combustible metals such as magnesium, titanium, zirconium, sodium, lithium, and
	potassium

A contractor under the supervision of Physical Plant inspects extinguishers monthly to ensure that each extinguisher:

- 1. is located in its designated place,
- 2. is not obstructed in access or visibility,
- 3. has visible operating instructions and nameplate,
- 4. has unbroken seals,
- 5. indicates pressure is in the operable range, and
- 6. has no physical damage, corrosion or leakage.

The inspection tag is dated and initialed every month. A contractor under the supervision of Physical Plant performs annual extinguisher maintenance and periodic hydrostatic testing in accordance with OSHA 29 CFR 1910.157.

B. Fire Blankets

Fire blankets are located in all teaching laboratories. Proper use of the fire blanket is explained by the laboratory supervisor at the beginning of each semester.

C. Emergency Showers/Eyewash Stations

All teaching and research laboratories in which hazardous substances are used are equipped with emergency showers and eyewash stations. Bottle-type eyewashes may only be used on a temporary basis if the proper eyewash is down for maintenance. The Department of Chemistry and Biochemistry lab coordinator flushes all eyewash stations and hand-held drench hoses once a week for at least three minutes. Department of Biology faculty and vivarium supervisor are responsible for flushing eye washes weekly in their own laboratories. Physical Plant tests safety showers twice a year.

Instructors of laboratory courses will describe the proper use of emergency showers and eyewash stations at the beginning of the semester.

D. First Aid Kits

First aid kits are located in each teaching and research laboratory and each stockroom. Departments are responsible for restocking first aid kits. Laboratories in which particular chemicals with special first aid requirements are used must be equipped to meet those special needs. For example, laboratories in which hydrofluoric acid is in use must stock 2.5% calcium gluconate for immediate treatment of skin contact. The faculty should discuss such special requirements with the EHS Office.

E. Spill Control Supplies

Spill response procedures are outlined in Chapter 14. Each lab should stock appropriate spill control supplies for the materials used in that lab. Spills should only be handled by trained personnel. Notify the Department Office when supplies are used so that they can be replaced as soon as possible. Replacing supplies is the responsibility of each Department.

Chapter 6: Standard Operating Procedures (SOPs)

Standard Operating Procedures (SOPs) are specific measures to be taken by anyone working with particularly hazardous substances or conducting high-risk procedures as defined in this chapter. There are two types of SOPs and both must be used where applicable:

- 1. Chemical SOPs, which outline precautions related to specific substances in order to control hazards, and
- 2. Laboratory-specific SOPs, which document procedures for the safe use, storage, and disposal of hazardous substances in a particular laboratory.

Principal investigators and laboratory supervisors are responsible for establishing SOPs for hazardous substances used under their direction and the laboratory spaces in which they and those whom they supervise work. The SOPs are to be used for training students and lab workers prior to working in a particular laboratory and prior to working with hazardous substances. Printed copies of the SOPs are kept in the laboratory's Safety Binder.

Hazard assessment

Prior to drafting an SOP, a hazard assessment should be performed to determine what kinds of hazards are present. The American Chemical Society publication, <u>Identifying and Evaluating Hazards in Research Laboratories</u>, may be used for guidance is assessing hazards (<u>https://goo.gl/fcslO7</u>). It has a detailed process for the structured development of SOPs that includes the risk assessment process. This process is intended to identify all potential hazards and determine which hazards warrant control. Hazard Assessment Matrices F-2 and F-3 from this publication are in Appendix C.

Chemical-specific Standard Operating Procedures (SOPs)

A Chemical SOP should describe the procedures and precautions necessary for handling a particularly hazardous substance. This includes special handling procedures, engineering controls, containment devices, decontamination procedures, personal protective equipment, and waste disposal.

Determining if a Chemical SOP is required

If a substance carries the GHS signal word, "DANGER," that substance should be assessed for the need for an SOP. The GHS signal word assigned to a substance can be found on the manufacturer container label, as well as the SDS. Whether an SOP is warranted should be based on risk and complexity of use, as determined by the judgment of the supervising faculty member. In general, an SOP should be written when the general safe-use guidelines for common hazard classes (corrosives, flammables, oxidizers) outlined in the Chemical Hygiene Plan are not sufficient to protect users of a particularly hazardous substance. In addition, SOPs are necessary for substances with specific first-aid treatments or antidotes. Substances that are widely used in a standardized way, such as acrylamide, should have SOPs.

Substances that fall under certain GHS hazard classes must have SOPs. The GHS hazard class(es) assigned to a particular substance can be found on its SDS. These GHS hazard classes that require SOPs are listed in Tables 6.1 and 6.2 below. Both GHS Acute Toxicity categories 1 and 2 require SOPs.

GHS Acute Toxicity Hazard Class	Category 1	ry 1 Category 2	
Acute Toxicity, Oral (mg/kg) - LD50	≤ 5	> 5	≤ 50
Acute Toxicity, Dermal (mg/kg) - LD50	≤ 50	> 50	≤ 200
Acute Toxicity, Inhalation - Gases (ppm) - LC50	≤ 100	> 100	≤ 500
Acute Toxicity, Inhalation - Vapors (from liquid) (mg/l) - LC50	≤ 0.5	> 0.5	≤ 2.0
Acute Toxicity, Inhalation - Dust & Mist (solids) (mg/l) - LC50	≤ 0.05	> 0.05	≤ 0.5

Table 6.1: GHS Acute Toxicity hazard classes requiring SOPs

Table 6.2: Other GHS hazard classes requiring SOPs

GHS Hazard Class	SOP Criteria	Hazard Statement
Flammable gases /	Category A	May react explosively even in the absence of air
chemically unstable gases		
Flammable Solids	GHS	Flammable Solid
	Category 1	
Pyrophoric Liquids	GHS	Catches fire spontaneously if exposed to air
	Category 1	
Pyrophoric Solids	GHS	Catches fire spontaneously if exposed to air
	Category 1	
Self-Heating Substances and	GHS	Self-heating; may catch fire
Mixtures	Category 1	
In contact with water emit	GHS	In contact with water releases flammable gases
flammable gases	Category 1	which may ignite spontaneously
Self-Reactive Substances	Type A and	Heating may cause fire and explosion
	В	
Explosives	GHS Division	Mass Explosion Hazard
	1.1	
Explosives	GHS Division	Projection Hazard
	1.2	
Explosives	GHS Division	Fire hazard, minor blast hazard or minor
	1.3	projection hazard

Substances that fall outside of the criteria in Tables 6.1 and 6.2 may still warrant having an SOP. If a particular substance does not meet the specified criteria, SOPs are to be used at the discretion of the supervising faculty member.

The template for a Chemical SOP can be found in Appendix A, along with an example SOP from the ACS manual referenced above. The template is available online on the PC EHS webpage.

Chemical SOPs stored in laboratory Safety Binders and electronically archived must include a copy of the substance's SDS and any appropriate supporting documents, e.g., experimental procedure(s), hazard assessment, product safety bulletins, etc.

Laboratory-specific Standard Operating Procedures (SOPs)

Each laboratory where hazardous substances are handled must have an SOP for the room. It should include procedures, instructions, and precautions for the handling and storage of hazardous substances and the proper use of equipment located in that that laboratory. A floor plan should be attached, showing locations of all emergency and safety equipment and spill supplies.

The template for a Laboratory SOP can be found in Appendix B. It is available online on the PC EHS webpage.

It is recommended that the Risk Assessment matrices F-2 and F-3 in <u>Identifying and</u> <u>Evaluating Hazards in Research Laboratories</u> be completed prior to drafting a Laboratory SOP. These matrices contain sections describing possible hazards that may be specific to a laboratory and provide guidance to help ensure that no hazards are overlooked.

Peer review

Chemical SOPs must be reviewed by a colleague within the Department prior to working with the hazardous substance. The faculty member reviewing the SOP shall sign and date the SOP to document his/her acceptance of it. Laboratory SOPs should be reviewed by other faculty members using the space.

Storage of SOPs

Each lab will have a Safety Binder that acts as a storage location for SOPs. Printed copies of all SOPs (Laboratory and Chemical) along with their associated attachments are stored in the Safety Binder.

Each SOP, along with all supporting documents, will be electronically archived in a publicly accessible location online. Each lab will have an electronic folder with all SOPs for that lab. In addition, a central repository for all SOPs developed for use at PC will be maintained in a publicly accessible location online.

Electronic inventory

All substances that require SOPs will be flagged in the Chemical Inventory System (CIS) (see chapter 8) by the faculty member adding it to the inventory. For each substance requiring an SOP, a link shall be provided in the CIS to that SOP.

Training and documentation

SOPs are to be used for training students and lab workers prior to working in a particular laboratory and prior to working with any substance with an SOP. Principal investigators and laboratory supervisors must review the SOPs with students and/or lab workers. A signature page attached to each SOP is to be used to document this training.

Research laboratories

Principal investigators and laboratory supervisors must review the Laboratory SOP with students prior to their work in the lab and on an annual basis thereafter. Principal investigators and laboratory supervisors must review Chemical SOPs with students prior to their work with hazardous substances and on an annual basis thereafter. The training is to be documented on the signature page. The signature page will be scanned and stored electronically in a training documentation folder any time new signature(s) are added.

Teaching laboratories

The content of Laboratory SOPs should be distributed to students, and training conducted, before coursework begins. The content of Chemical SOPs should be distributed to students, and training conducted, before working with the substance. Training must be properly documented.

6: Standard Operating Procedures

Electronic copies of all training records are to be kept by EHS indefinitely. Printed copies of training records in the Safety Binders are to be kept for at least 1 year.

Chapter 7: Container Labeling

Container labels are a primary means of communicating hazard information. Manufacturers are required to assess the hazards of the chemicals they provide and to display health and physical hazard information on the containers. They are required to use the Globally Harmonized System (GHS) of labeling to convey hazard information on containers. Anyone who works with hazardous substances should have training that explains the GHS labeling system. GHS uses pictograms to communicate specific information about hazards. It is recommended that a poster be displayed in each lab that explains the nine GHS pictograms.

Health Hazard	Flame	Exclamation Mark	
	(19)		
 Carcinogen Mutagenicity Reproductive Toxicity Respiratory Sensitizer Target Organ Toxicity Aspiration Toxicity 	 Flammables Pyrophorics Self-Heating Emits Flammable Gas Self-Reactives Organic Peroxides 	 Irritant (skin and eye) Skin Sensitizer Acute Toxicity (harmful) Narcotic Effects Respiratory Tract Irritant Hazardous to Ozone Layer (Non-Mandatory) 	
Gas Cylinder	Corrosion	Exploding Bomb	
\diamond	A REAL		
• Gases Under Pressure	 Skin Corrosion/ Burns Eye Damage Corrosive to Metals 	• Explosives • Self-Reactives • Organic Peroxides	
Flame Over Circle	Environment (Non-Mandatory)	Skull and Crossbones	
(*		
• Oxidizers	Aquatic Toxicity	• Acute Toxicity (fatal or toxic)	
For more information: Occupational Safety and Health Administration			
www.os	U.S. Department of Lab ha.gov (800) 321-OS	or 6HA (6742)	

Figure 7.1: GHS Pictograms and Hazards

A. Manufacturer Containers

Manufacturer labels on containers should not be removed or defaced while the container has the original product in it. Faculty members should amend any label, either with words and/or GHS pictograms, that does not disclose important hazards. Hazards can be determined from a GHS-compliant Safety Data Sheet (SDS). Sigma-Aldrich posts GHS-compliant SDSs for most hazardous substances online. Another source of information is the supplier of the material, who is required by law to provide this information.

B. Secondary Containers

Secondary containers used for storing substances (e.g., beakers, flasks, bottles, etc.) must be labeled to indicate the contents and the hazards present. The hazards may be indicated by using words and/or GHS pictograms.

Marking pens used to indicate the contents of the container must be resistant to the contents of the container. Alternatively, the label should be covered with clear tape to prevent chemical drips from smearing the label. If reusing an empty manufacturer bottle as the secondary container, the original label must be removed or covered.

C. Other Labeling Considerations

If a container is too small for its label to indicate necessary hazard information, a sign or label in the area where it is stored must communicate that information. Furthermore, this sign or label must clearly indicate the identity of the container to which it applies. This might be achieved by posting a sign on the shelf, cabinet, or refrigerator in which the small container is stored or labeling a larger container that houses the small container. Hazard information for multiple small containers with the same hazard can be indicated in a similar fashion.

Unknowns for instructional use should be labeled with the hazards of the constituents or the hazards must be otherwise communicated to those handling the samples.

Chapter 8: Chemical Storage, Inventory, and Transportation

Management of chemicals, including storage, inventory, and transportation, is an important aspect of chemical safety. The following general guidelines should be followed. Additional management requirements for specific hazard classes are discussed in the chapters of Section 2 that address those specific hazards.

A. Compatible Chemical Storage

Chemicals should always be segregated into compatible groups during storage to prevent hazardous reactions in the event of an accident. When substances are stored by physical hazard class (flammable, oxidizer, acid, base, water reactive, etc.), the areas and/or shelves should be clearly labeled to indicate the hazard. The major laboratory chemical distributors have established color coded systems for chemical storage based on compatibility. Be aware that the systems vary somewhat between distributors.

The table in Appendix I provides examples of incompatible chemicals. This table is not exhaustive. Consult Safety Data Sheets (SDS) for information regarding chemical compatibility and safe storage conditions.

In addition to the segregation guidelines in Appendix I, inorganic and oxidizing acids must be separated from organic compounds, including organic acids and other combustible materials. Nitric acid (>40%) must be segregated from other inorganic acids. Glacial acetic acid is combustible and should be stored with flammable and combustible materials.

Secondary containment devices such as tubs, trays, beakers, or buckets reduce the chance that incompatible chemicals will come into contact with each other. Secondary containers should have enough capacity to hold 100% of the contents of the largest container stored in them. The material of the secondary containment should be compatible with the substances stored within it. Polypropylene trays or bins are suitable for most purposes.

Water reactive materials should not be stored under sinks. As an added precaution, water reactives can be stored on trays or other secondary containers filled with sand.

B. Storage Areas

Storage areas should be isolated from working areas whenever possible. Exposure to heat or sunlight should be avoided; and storage areas for volatile chemicals should be ventilated when feasible. Shelving should be sturdy and firmly anchored. Shelving should also be compatible with any potential spilled liquid. Chemical containers should have caps and lids tightly closed and no spilled residue should be on the outside of the container. Storage areas

should be checked frequently to ensure that labels are properly affixed to the container. Loose labels should immediately be taped on using clear packing tape.

Bench tops should not be used for storage, and where possible, hazardous substances should not be stored on shelves between bench tops or above shoulder height. Storage of chemicals in or near sinks where there is access to drains is prohibited.

Vacuum pumps should never be used near any combustible or flammable materials, such as solvents. If you do use the vacuum pump in a cabinet, the cabinet should be designed for this use. Nothing may be stored in the cabinet except non-combustible vacuum pump oil.

Refrigerated storage of flammable materials is only allowed in refrigerators or freezers designed for and UL approved for storage of flammable materials.

Storage of chemicals in fume hoods and biosafety cabinets can severely diminish their effectiveness and is discouraged. Storage of chemicals in fume hoods should be reduced to a minimum and should not clutter the hood or interfere with airflow or other operations in the hood. Hoods used to store noxious or acutely hazardous materials should be designated solely for storage and labeled with a sign stating so.

Consider storing larger containers (4 liters or more) in a chemical storage room or appropriate storage cabinet. If containers must be stored on the floor, they must be placed within adequately-sized secondary containment capable of holding 100% of the contents of the largest container stored.

When chemicals are moved from one storage location to another, the chemical inventory should be updated.

C. Chemical Inventory

Each Department maintains an inventory of chemicals. These inventories should be updated at least annually. Faculty and staff members should check the inventory to ensure that the substance is not already available prior to submitting orders to the Department office.

D. Transportation of Chemicals

A bottle carrier or cart should be used to transport containers of hazardous chemicals larger than one liter from one storage location to another. The chemical inventory should be updated as chemicals are moved between storage locations. When transporting hazardous chemicals through hallways, wear one glove, leaving the other hand free to open doors, press elevator buttons, etc.

Chapter 9: Laboratory Waste

A. Defining Hazardous Waste

All waste generated in the laboratory must be disposed of properly. Hazardous waste is subject to strict regulatory requirements to document and ensure its proper disposal. Federal (EPA 40 CFR 261) and Rhode Island regulations define various categories of hazardous waste. Regulatory lists for the following waste categories are included in Appendices L - O.

- Hazardous chemicals: U wastes
- Acutely hazardous chemicals: P wastes
- Solvent waste: F wastes
- Characteristic wastes: D wastes
 - Ignitable
 - Corrosive
 - Reactive
 - \circ Toxic
- Rhode Island wastes: R wastes

Faculty members are responsible for determining if waste generated in their laboratories is hazardous waste. Records must be kept of waste determinations. Records may be in the form of descriptions on hazardous waste labels, waste inventory logs, waste disposal procedures in a laboratory handout, notes in a research notebook, or equipment logs documenting materials tested. The Chemical Hygiene Officer can assist with evaluation of laboratory waste.

B. Disposal of Non-Hazardous Waste

A "non-hazardous waste" is a waste that does not meet the criteria listed above for "hazardous waste;" the method of disposal varies depending on its form and properties. Solid waste must be labeled "non-hazardous" and can then be put in the laboratory trash. Liquids that are not water-soluble must be solidified (absorbed) and disposed of as a solid as described above. Water-soluble liquids may be flushed to the sewer if they meet BOTH of the following criteria, so long as they are flushed on an as-generated basis:

- 1. The pH of the waste is between 5 11.
- 2. The waste does not contain any bloodborne pathogens, carcinogens, reproductive toxins, or toxic organic compounds.

In a situation where a water-soluble liquid waste cannot go down the drain because it does not meet the above criteria, it shall be labeled "non-hazardous waste" and placed in one of the main accumulation areas. Ensure that the label identifies the contents.

C. Hazardous Waste Collection in the Lab

Hazardous waste generated in the laboratory is collected in satellite waste containers, which must be kept at or near the point of generation in a Satellite Accumulation Area. All satellite waste containers should have screw top lids and be compatible with the waste they hold. All satellite waste containers should have a "Hazardous Waste" label affixed before waste is introduced to the container. The label pictured on the right should be used for this purpose. Labels are available from the Department office.

When adding waste to the satellite container, the following information must be added to the label right away:

- The generic names of the principle hazardous components (no chemical formulas, structures or abbreviations may be used)
- The hazard classification (e.g., corrosive, ignitable, oxidizer, toxic, reactive)

Indelible markers should be used for labeling. Satellite containers must be kept closed except when waste is being added.

REFER TO LABELING INSTRUCTIONS ON REVERSE
HAZARDOUS
WASTE FEDERAL LAW PROHIBITS IMPROPER DISPOSAL If found, contact the nearest police or public safety authority or the US Environmental Protection Agency.
CONTENTS USE FULL CHEMICAL NAME
DATE:///
PROVIDENCE COLLEGE PROVIDENCE, RI 02918 EPA I.D.# RID075704601

To minimize the hazard of reactions from incompatible substances, wastes with different hazards that create physical hazards or undesirable reaction products should not be mixed.

When collecting waste in carboys, halogenated waste should only be collected in fluorinated HDPE carboys. Halogenated solvents can degrade the plastic in ordinary carboys, whereas fluorinated HDPE is chemically resistant to halogenated materials.

The amount of waste accumulated in the laboratory at any time should be minimized. Only one satellite waste container of a particular type of waste is allowed in the laboratory at any given time.

D. Hazardous Waste Removal from the Lab

When a satellite hazardous waste container is full (keep 2" of headspace at the top) or the waste will no longer be generated in the laboratory, the waste must be moved to a Main Accumulation Area within 3 days. Only persons who have completed hazardous waste training are permitted to transport waste containers. Main Accumulation Area locations:

Chemistry: Albertus Magnus 201, 205, 216, 315 Biology: Albertus Magnus 305

When a container is moved to a Main Accumulation Area, the date must be added to the label. Never remove the label under any circumstances. Always check containers to make sure they are properly closed and that the labels are complete and legible.

E. Hazardous Waste Storage and Disposal

Upon receipt at the Main Accumulation Area, all waste is separated and stored by hazard category. To minimize the potential for releases, waste containers may be placed in trays or other secondary containers.

Wastes are shipped off-site using a licensed hazardous waste transporter. All hazardous waste is taken to licensed facilities that treat, recycle, incinerate, or otherwise dispose of the materials using EPA approved methods for the particular waste type.

F. Biohazard and Sharps Waste

Biohazard waste is anything under the "regulated medical waste" definition in the Rhode Island DEM Medical Waste Regulations (see Appendix P). All biohazard waste is to be disposed of in biohazard boxes. When full, the biohazard boxes are sealed with tape and placed in the hallways for collection. It is the responsibility of the Department that generated the biohazard waste to create a work order to have Physical Plant pick up the box. Biohazard boxes are not to be filled to more than 45 lbs.

Sharps waste (as defined in the Rhode Island DEM Medical Waste Regulations in Appendix P) must be disposed of in designated biohazard sharps containers. These containers are not to be filled more than $\frac{2}{3}$ full, at which point they must be closed and placed within a biohazard box for disposal.

G. Disposal of Empty Containers

The hazardous waste regulations define an empty container as a container from which everything that can be poured out has been removed, and no more than one inch of material residue remains.

Most empty containers can be safely and legally disposed of as regular trash with the exception of "Acutely Hazardous Waste" containers. Empty containers that contained "P" listed, acutely hazardous chemicals should be handled as hazardous waste. Alternatively, these containers can be triple rinsed with an appropriate solvent, and the solvent disposed of as hazardous waste. The empty container may then be discarded in the regular trash.

Empty glass containers must be placed in a container designated for broken glass, even if they are not broken; plastic containers may be placed in the recycle bin.

H. Disposal of Broken Glass

Broken glass must be placed in a container designated for broken glass. Physical Plant will discard these containers in such a manner as to avoid injury. The Department administrative assistant will contact Physical Plant to arrange a pickup, and the Department will supply a new box.

I. Disposal of Unknowns

It is extremely difficult and costly to identify the contents and hazards of unlabeled materials. As discussed in Chapter 7, it is crucial that maintaining labels be a standard laboratory practice. If you do have unknowns, contact the Chemical Hygiene Officer immediately upon their discovery.

J. Waste Inspection

The appropriate laboratory coordinator inspects the Main Accumulation Areas weekly when waste is present and corrects any deficiencies found immediately. A written record of these inspections is to be kept in the lab's Safety Binder.

K. Training

The EHS Office provides annual training to all waste generators and handlers.
Chapter 10: Laboratory Closure Procedures

When a laboratory is closed down, proper laboratory closure procedures should be followed to facilitate the transition of research and teaching lab space to new faculty members. This procedure ensures that hazardous wastes, unknown chemicals, unlabeled material, etc. are not left behind. The departing faculty member must contact EHS to arrange an inspection in advance of his/her departure, and the Chair must ultimately approve the condition of the laboratory.

- Research lab space should be completely emptied of chemicals, unless the next PI using the space designates chemicals that s/he intends to use. The remaining chemicals should either be brought to Central Storage or disposed of appropriately. The Central Storage area should not be treated as a repository for the departing PI's old supplies.
- 2. All chemicals in Central Storage belonging to the departing faculty member should be assessed. Any hazardous substances that do not pose any short-term value to the rest of the faculty should be disposed of appropriately.
- 3. Reagent bottles and other chemical containers that are left behind should be clearly labeled including all necessary hazard labeling. No formulas or shorthand notations are permitted, except for synthesized materials where formulas are necessary.
- 4. Old equipment that the Department no longer needs should be removed from the lab.
- 5. Verify that there are no chemical spills or spill residues, or any other overt contamination left in the laboratory.

Before faculty members depart on sabbatical leave, all research areas under their supervision should be thoroughly cleaned, and any shared equipment and apparatus returned to storage locations as appropriate. The faculty member should contact EHS to arrange an inspection of the research areas under his/her supervision.

Chapter 11: Laboratory Access and Usage

A. Laboratory Working Alone and After Hours Policies

These policies apply to laboratory work in the Providence College science laboratories, located in Albertus Magnus Hall, Sowa Hall, and Hickey Hall. Departments or individual faculty members may establish more restrictive policies for spaces under their control.

Laboratory working hours defined

Weekdays

Working in laboratories from **7 am to 6 pm** is defined as working during "**regular hours**". Working in laboratories from **6 pm to 11 pm** is defined as working "**after hours**". Working between **11 pm and 7 am** is defined as "**restricted hours**".

Weekends and holidays

Working any time in laboratories on weekends and holidays is defined as working "after hours". Working between 11 pm and 7 am on weekends and holidays is defined as "restricted hours".

Student teaching laboratories

Students may work in a teaching laboratory outside of the regular laboratory periods, but during regular hours only with the permission of the instructor, who is responsible for ensuring that the students receive sufficient instruction to work safely. When doing so, students are encouraged to check in with their Department office prior to working in the laboratory.

Faculty and staff laboratory work

There are no restrictions on the use of laboratories by faculty members or technical staff. They are expected to avoid working alone whenever possible and to use good judgment about performing hazardous procedures when working alone. This in no way implies that other safety requirements are waived; on the contrary, the use of good judgment implies expert knowledge of safe procedures and practices.

Student research laboratories

A student may use laboratory facilities for independent research only after the Principle Investigator (PI) has reviewed the experimental procedure(s) and any associated hazards, and has determined that the student possesses adequate training in proper experimental and emergency procedures. Students are responsible for performing all their work in accordance with those procedures and must report all accidents, chemical spills, and unsafe conditions immediately to the PI.

In addition, research students working with chemicals must satisfactorily complete laboratory safety training provided by the EHS Office. The PI will be responsible for forwarding the names of students working with chemicals to EHS to schedule training.

Independent research students who are conducting laboratory procedures during regular hours (7 am-6 pm) are encouraged to check in with the PI or his/her designee before working in the laboratory. Students must have written permission from the PI prior to working after hours in a laboratory (see the "Permission to Work After Hours" form in Appendix E). Completion of the form, with the PI's signature, allows students after-hours access to the laboratory for a 12-month period. The form must be re-submitted if the nature of the work changes, the PI changes, or the PI permits a 12-month after-hours extension. The permission form must be kept on file in the PI's Department office and a copy sent to the EHS Office.

The PI shall be responsible for determining the health and safety risks associated with student research. The PI shall indicate on the "Permission to Work After Hours" form whether a student's research is classified as "High" or "Low" risk. If a student's research is classified "High" risk, s/he will be required to work using the "buddy" system. Students serving in a "buddy" capacity must be approved to work after hours, be within hearing distance of each other, be familiar with emergency procedures, and be aware that s/he is serving in the "buddy" capacity.

Each semester, and during summer break, the PI will notify Business Services to grant card access to the students approved to work after hours, and the Department Chair will submit a list of approved after hours research students to the Office of Safety and Security. If Security identifies a student working after hours not found on the approved list, the student will be escorted from the building. Research students who fail to comply with the College's Laboratory Working Alone and After Hours Policies may have their laboratory privileges suspended or revoked.

Student research in laboratories during restricted hours, **11 pm and 7 am**, is discouraged except when necessary, and requires authorization from the PI. Faculty permission must be noted by checking "Yes" in the "Restricted Access Allowed" section of the "Permission to Work After Hours" form.

Students approved to work during restricted hours, <u>regardless of their risk category</u>, are required to call and check in with the Security Office every hour and upon leaving the building for the evening. Laboratory phones are available in the labs along with Security's phone number. Students who fail to provide notification will be contacted via cell phone by Security.

B. Visiting Researcher Policy

This policy covers temporary laboratory access for visiting professors as well as all non-PC graduate students and lab assistants. It spells out the credentialing and approval procedure for laboratory and equipment use.

To support Providence College's efforts, generally, regarding security within campus buildings, and to ensure, specifically, the safety of those performing tasks in College laboratories, all NON-PC researchers working in campus laboratories are required to obtain written approval from the sponsoring faculty member <u>prior</u> to working in the laboratory. The procedures outlined in this section are meant to manage access to PC laboratories, to help ensure safety and accountability for persons engaged in lab-related activities, and to provide basic knowledge of emergency response protocol. Therefore, lab-safety training, including safety-related training specific to the research, must be completed as a condition of approval. This training should include all relevant laboratory and chemical-specific SOPs (see Chapter 6) as necessary.

Approved non-PC researchers are only allowed access to PC laboratories during hours permitted by the sponsoring faculty member. While on the PC campus, approved researchers shall carry a photo ID.

The Visiting Researcher Form (see Appendix F) must be completed before any non-PC researcher gains access to any labs.

To obtain laboratory- and equipment-use approval, the Visiting Researchers must:

- 1. Contact EHS at <u>ehs@providence.edu</u> for access to online safety training. A completion certificate will be emailed to you. Print out this certificate and submit it to your sponsoring faculty member.
- 2. Sign the Voluntary Waiver Form provided by the sponsoring faculty member.
- 3. Complete lab-specific safety and equipment training provided by the sponsoring PC faculty member.

The sponsoring faculty member must:

- 1. Provide EHS contact information to the applicant in order to arrange online safety training, and instruct the applicant to print out and bring in the completion certificate(s).
- 2. Complete a Visiting Researcher Form for the applicant; have him/her sign the form when s/he arrives.
- 3. Provide lab-specific safety and equipment training to the visiting researcher.
- 4. Ensure that the visiting researcher signs the Voluntary Waiver Form.
- 5. Submit the Visiting Researcher Form, Waiver Form, and training certificate(s) to the Department Chair for approval and signature.

The Department Chair must:

- Review the Visiting Researcher Form. Make sure that lab-specific training, EHS online safety training (as documented by the attached training certificate), and the Voluntary Waiver Form have been satisfactorily completed. A copy of the Visiting Research Form should be sent to EHS.
- 2. To grant Department approval, sign and date the Visiting Researcher Form.
- 3. File all documents in the Department office. These forms must be maintained on file for three years from the last date of access to the lab.

The EHS Office must:

- 1. Provide the visiting researcher with the appropriate online safety training course(s) and certificate(s).
- 2. File a copy of the Visiting Researcher Form sent from the Department Chair after approval is granted.

Chapter 12: Laboratory Inspections

Laboratory inspections are conducted to identify and correct potential health and safety hazards that could pose an unreasonable risk to laboratory personnel, students, and the community. The inspector should identify potential regulatory non-compliance issues, and identify areas where maintenance of safety equipment may be needed.

EHS inspections

EHS conducts annual inspections of laboratories and other facilities in which hazardous substances are used. Results of EHS inspections are provided to faculty members and the Department Chair shortly after the inspection.

Faculty inspections

Faculty members or designated laboratory personnel are responsible for performing selfaudit safety inspections at least annually. The self-audit inspection form is attached as Appendix J. The completed form should be kept in the lab's Safety Binder, and copies should be sent to the EHS Office and the Department Chair. Deficiencies and corrective actions are to be noted, with a date by which they are expected to be corrected. Serious deficiencies should be corrected immediately, and minor issues within two weeks. Follow-up notification is to be provided to the EHS Office when all deficiencies are corrected.

The EHS Office issues a schedule of laboratory inspections at the beginning of each semester. Faculty members responsible for those laboratories are to have the self-audit completed, including any necessary corrective actions, by the end of the semester.

These inspection reports must be kept on file at the EHS Office for at least three years, and in the lab's Safety Binder for at least one year.

Chapter 13: Laboratory Safety Training

A. Employee and Research Student Training

Under the OSHA Laboratory Standard all employees working in laboratories must receive specific information and training regarding the requirements of the Standard, chemical hazards, handling methods, and emergency procedures. Employees include anyone who receives compensation from Providence College for their services; this includes the faculty, staff, and students on work-study or grant funded stipends. Students doing independent research must also receive this training.

New faculty and staff members shall meet with the Chemical Hygiene Officer to review the requirements of the Chemical Hygiene Plan.

Training of students who will conduct research has two components, individual instruction by the faculty member with regard to specific hazards, handling procedures and emergency procedures in their laboratory (lab-specific training), and general training provided by the Chemical Hygiene Officer to review Plan requirements. Training must be accomplished prior to working with hazardous substances in the laboratory, and at least annually thereafter.

The EHS Office conducts annual Hazardous Waste training for all faculty and staff members as required by the state of Rhode Island and federal regulations.

Animal Care training is required for anyone working with animals covered under an IACUC protocol. Medical clearance is also required for research students. Full details are covered in the College's Animal Occupational Health & Safety Program.

Bloodborne Pathogen training for Department of Biology faculty members teaching Anatomy labs where dissections with sharp instruments will take place will be held annually. Training may be required for any other faculty or staff members depending on their work, at the discretion of the EHS Office.

The Chemical Hygiene Officer will keep documentation of all annual training.

B. Student Training

Faculty members are responsible for providing safety information and training to their students including:

- the hazards of the chemicals being used,
- safe handling procedures,
- use of personal protective equipment,

- emergency procedures (see Chapter 14), and
- sources of additional information (e.g., labels, SDS, safety publications, this Chemical Hygiene Plan).

If an experiment involves the use of a chemical that requires a Standard Operating Procedure (SOP), the student will be familiarized with the SOP for the use of that chemical and specific experimental procedure. This training will be documented in the lab's Safety Binder. If the experiment involves the use of a select carcinogen or reproductive toxin (see Chapter 22), specific notification must be given to the student.

At the beginning of each semester in laboratory courses, the supervising faculty member must indicate the location of safety showers, eyewash stations, fire blankets, emergency exits, pull boxes, and evacuation routes.

Students enrolled in Department of Chemistry laboratory courses must sign a "Chemistry Laboratory Safety Agreement" prior to working in the laboratory. Agreements are kept on-file in the Department office.

C. Special Requirements for Formaldehyde

The OSHA Formaldehyde Standard requires annual training for all users of formaldehyde-containing products containing greater than 0.1% formaldehyde or products that are capable of releasing in excess of 0.1 ppm formaldehyde. Faculty members are responsible for training those using formaldehyde-containing products under their supervision. The training must include:

- a discussion of the contents of the regulation (required for employees only) and the SDS,
- a description of the potential health effects of and symptoms of exposure,
- reporting requirements for symptoms of exposure,
- a description of safe work practices and engineering controls (e.g., fume hoods),
- the purpose of personal protective equipment (e.g., goggles and gloves), and
- instructions for handling emergencies.

All this information is included in the Formaldehyde SOP in Appendix D, which is to be used to conduct this training. Training is to be documented in the lab's Safety Binder.

Chapter 14: Emergency Procedures

A. Emergency Planning

Effective emergency response requires pre-emergency planning. It is the responsibility of each faculty member to evaluate the hazards of the experiments being performed, to determine appropriate emergency procedures, and to ensure that all employees and students are aware of those procedures.

Emergency Telephone Numbers		
When dialing from a campus phone to an outside line, dial 9 first.		
All campus phone numbers are preceded by 865 when dialing from a mobile phone.		
Providence College EMERGENCY NUMBER	2222	
City Emergency Center	911	
PC Security (non-emergency)	2391	
Student Health Center	2422	
Physical Plant	2166	
Environmental Health and Safety	2549 or 1585	
Poison Control Center	1-800-222-1222	

Emergency response equipment

Easy access to emergency equipment is essential to quick response. Emergency response equipment (fire extinguishers, fire blankets, eyewash stations, safety showers, first aid kits, spill response supplies) should never be blocked. A quick check should be made whenever entering the laboratory to ensure access to emergency response equipment is clear. Any obstructions should be removed immediately. If any equipment is missing or damaged, it should be reported immediately to the Physical Plant, and Security will also be notified if equipment is stolen. Faculty members should determine the appropriate extinguishers for their laboratories (see Chapter 5).

Instructors must indicate the locations of fire blankets, safety showers, and eyewash stations to students at the beginning of each semester, and Principle Investigators (PIs) must indicate their locations to all new workers under their supervision.

Emergency exits and evacuation plans

Ready access to all exits must be maintained. Aisle space must be maintained to ensure ready access to exits. Exit signs designating all exits from the building and hallways are equipped with emergency lighting. These lights are on emergency power in the event of a power failure. Instructors must inform students of the location of emergency exits and of evacuation routes at the beginning of each semester, and PIs must indicate their locations to all new workers under their supervision.

Emergency communication

Emergency alarm pull boxes are located on all levels of the science complex. These boxes sound an alarm throughout the building, signaling evacuation, and directly alert the Fire Department. If possible, the campus emergency number, 2222, should be called from a telephone a safe distance from the emergency to provide Security with details. Security will respond and coordinate other emergency services.

Instructors must inform students of the location of emergency alarm boxes at the beginning of each semester, and PIs must indicate their locations to all new workers under their supervision. Faculty members must also inform them that immediate evacuation via the nearest exit is mandatory upon hearing the alarm.

A sign indicating whom to contact for information on the chemicals and hazards of a particular laboratory, in the event of an emergency, is posted on every laboratory door. The faculty member assigned to the room is responsible for keeping signs up-to-date. All chemical stockrooms are identified with NFPA diamonds.

Chemical emergencies

Faculty members should evaluate the hazards and quantities of the chemicals in use in their laboratories to determine what level of response would be required in the event of a chemical release. All employees and students must be informed of any emergencies that would require immediate evacuation of the room or building. The appropriate faculty member or Department laboratory coordinator ensures that each laboratory has, or has ready access to, the appropriate spill response supplies at the beginning of each semester. The EHS Office can provide assistance in evaluating specific hazards and appropriate emergency response procedures upon request.

<u>Utility loss</u>

Each Department should keep up-to-date procedures to be followed in the event of power or water loss (e.g., equipment shut-off). Emergency power outlets are clearly labeled in each building. In the event of power loss, no operations releasing hazardous vapors should be conducted as ventilation is not available. In the event of water loss, no hazardous substances can be used in the laboratory as emergency eyewashes and showers are not available.

Special needs

Faculty members should discuss evacuation procedures with all mobility-impaired persons in the laboratory to determine their needs for assistance.

B. Emergency Procedures – Basic Steps

The first priority in emergency response is the protection of life and health. The following four basic steps apply to all emergency situations. Additional procedures for specific situations follow.

- 1. Ensure that everyone in the immediate vicinity is aware of the problem.
- 2. Contain the emergency if it can be done safely.
- 3. Pull the alarm to evacuate the building if the emergency cannot be contained or there is any doubt as to the severity of the situation.
- 4. Summon Aid Campus Security Emergency Number is 2222.

C. Fires

Many small laboratory fires can be controlled by removing the source of ignition, dousing with water or sand (**do not apply water to chemical fires**), or smothering the flame with a watch glass or beaker to eliminate the oxygen needed to sustain the fire. Fire extinguishers, while present in all Albertus Magnus labs and Hickey hallways, should only be used when there is limited risk of the fire spreading. If the fire cannot be extinguished using the immediate measures mentioned above, the following actions should be taken.

- 1. If your body, clothing, or hair is on fire: drop to the floor and roll, use the deluge shower, or use a fire blanket to extinguish the flames.
- 2. If the fire is in a hood, close the sash.
- 3. Pull the alarm to signal evacuation.
- 4. Evacuate the building.
- 5. Assist Security and the Fire Department by providing them with information on the exact location of the fire, hazards in the area, and location of emergency shutoffs.

Upon hearing the fire alarm, laboratory occupants should: shut off ignition sources, turn off the lights, close the laboratory door when everyone is out, and immediately exit the building using the nearest exit. Everyone should proceed to the designated rally point shown on the evacuation route maps in each lab. Faculty members should confirm that all students under their supervision are outside. No one should leave the area unless specifically told to by Security.

D. Personal Injury

In the event that someone is injured, take the following actions. Additional procedures for responding to chemical contamination are listed below.

- 1. Seek the assistance of a faculty or staff member.
- 2. Rescue the victim from life-threatening danger if it can be done safely.
- 3. For minor injuries, treat with local first aid supplies and, if necessary, call Security at 2222 for transport to the Student Health Center. All Security officers have first aid training.
- 4. For serious injuries, call Security at 2222 and request an ambulance for transport to a local medical facility.
- 5. Contact the supervising faculty or staff member.
- 6. Clean up or control any hazardous condition that caused or was caused by the accident if it can be done safely. See Section E (Chemical Releases) below.

Chemical contamination

In the event of eye contamination take the following actions:

- 1. Go immediately to an eyewash station and flush the eye for at least **15 minutes** (the 15 minute flushing time is essential to prevent damage to the eyes).
- 2. The eyes should be held open (remove contact lenses).
- 3. Call Security for assistance at ext. 2222.
- 4. Medical attention is required for <u>all</u> cases of eye contamination.

In the event of skin or clothing contamination take the following actions:

- 1. Use the safety shower, or laboratory sink to thoroughly flush the area (do not go to the restroom to wash).
- 2. Remove <u>all</u> contaminated clothing. If the head has been contaminated flush well prior to removing safety goggles so that contaminants are not flushed into the eyes.
- 3. Call Security at ext. 2222 to report the incident and receive assistance.
- 4. In cases of visible tissue damage, contamination of a large area, or contamination with an acutely toxic substance, medical attention is required. Security may transport directly to a local medical facility.

Injury reporting

All injuries, however slight, must be reported immediately to the supervising faculty member or, in the case of faculty accidents, the Department Chair. The *Student Injury Report Form* in Appendix G must be completed and submitted to the Department Chair and EHS Office within 48 hours. Employee accidents or work related illnesses must also be reported to Human Resources (ext. 2341) within 24 hours.

E. Chemical Releases

Chemical releases can be divided into two broad categories: emergency responses and incidental releases. An **emergency response** is an occurrence that results, or is likely to result, in an uncontrolled release of hazardous materials that requires a response effort by employees outside the release area or other designated responders (e.g., fire department, clean-up contractor). Situations generally resulting in emergency responses include:

- The release requires evacuation of the area
- The release poses, or has the potential to pose, conditions that are immediately dangerous to life and health
- The release poses a serious threat of fire or explosion
- The release required immediate attention because of imminent danger
- The release may cause high levels of exposure to toxic substances
- There is uncertainty that those working in the area can safely handle the hazard
- The situation is unclear or data is lacking on important factors

An **incidental release** is defined by one or both of the following criteria:

- The substance can be contained, absorbed, neutralized, or otherwise controlled at the time of release by those in the immediate release area or other laboratory personnel
- The release poses no potential safety or health hazard

While most chemical releases in the laboratory are incidental releases and can be controlled by laboratory ventilation and cleaned up by laboratory personnel with minimal risk, some releases can pose a fire hazard or health hazard to lab personnel and other occupants of the building. The following procedures for notification and spill cleanup should be followed to ensure the safety of all building occupants and minimize potential property damage.

Hazard assessment and response

- 1. Assess the situation and determine if a hazard exists to others in the area. The supervising faculty member or other nearby faculty member should assist in this determination if at all possible.
- 2. If the release is considered an incidental release, keep the area clear while the release is cleaned up. The EHS Office can assist in the cleanup if necessary. Report the incident to the EHS Office regardless.
- 3. If the release poses an immediate threat to human safety, pull the fire alarm to evacuate the building. The Director of Emergency Management will consult with EHS, the Department Chair, and the responsible faculty member to manage the Incident Command with the Fire Department.

- 4. If the release does not pose an immediate threat to human safety, but the release cannot be cleaned up safely, keep the area clear. The laboratory or the building may need to be evacuated depending on the circumstances. Security can assist if evacuation is necessary. Contact the EHS Office to organize any clean-up efforts.
- 5. If there is any doubt regarding the potential threat of a chemical release, contact the EHS Office to assess the hazard. The EHS Office will contact Security or any clean-up contactor if necessary.

Spill clean-up

An incidental release should only be cleaned-up by trained laboratory personnel using the procedure listed below. Spill response should only be done under the immediate supervision of the faculty member responsible for the laboratory or another faculty member.

- 1. Assign specific tasks and keep everyone else away from the area.
- 2. Obtain the supplies and equipment needed.
- 3. All persons involved in spill clean-up must wear protective equipment. The minimum level of protective equipment is
 - a. lab coat or coat apron
 - b. splash goggles
 - c. chemically resistant gloves compatible with spilled substance
- 4. Contain the spilled material to as small an area as possible.
- 5. Proceed to clean up the spilled material using absorbent, neutralizers, etc. If neutralizing, never add strong acids and bases together.
- 6. Collect all spilled material and contaminated material for proper disposal (see Chapter 9).

If the spill is an emergency response and outside assistance is needed, the EHS Office will contact outside resources for assistance.

Spill control supplies

Spill control supplies for use in cleaning up spills are located throughout Albertus and Hickey. The locations for various supplies in Albertus are listed in Table 14.1, and the locations for various supplies in Hickey are listed in Table 14.2.

-	
Spill control pads	Albertus 201 in cabinet 119 (Chem)
	Albertus 208, 209, 212, 304, 306, 307, 312 (Bio)
	Albertus 214 under fume hood next to eye wash (Chem)
	Albertus 216 in cabinet 55 (Chem)
	Albertus 314 under fume hood (Chem)
	Albertus 315 in cabinet 20 (Chem)
Spill control pillows	Albertus 201 in cabinet 119 (Chem)
	Albertus 209 (Bio)
	Albertus 216 in cabinet 55 (Chem)
	Albertus 315 in cabinet 20 (Chem)
Acid/base spill kits	Albertus 201 in cabinet 119 (Chem)
	Albertus 214 under fume hood next to eye wash (Chem)
	Albertus 216 in cabinet 55 (Chem)
	Albertus 314 (Chem)
Acid/base neutralizer	Albertus 131, 208, 209, 304, 312 (Bio)
Mercury spill kits	Albertus 201 in cabinet 119 (Chem)
	Albertus 315 in cabinet 20 (Chem)
Mercury wipes	Albertus 201 in cabinet 119 (Chem)
	Albertus 215 under sink (Chem)
	Albertus 315 in cabinet 20 (Chem)
HF spill pillows	Albertus 209 (Bio)
Vapor blanket sheets	Albertus 201 in cabinet 119 (Chem)
	Albertus 315 in cabinet 20 (Chem)
Sand	Albertus 201 in cabinet 119 (Chem)
	Albertus 214 under fume hood next to eye wash (Chem)
	Albertus 315 under prep table (Chem)
Vermiculite	Albertus 205 under balance table (Chem)
	Albertus 315 under prep table (Chem)
Sodium bicarbonate	Albertus 205 under balance table (Chem)

Table 14.1: Location of spill control supplies in Albertus Magnus Hall

Table 14.2: Location of spill control supplies in Hickey Hall

1 11	<u> </u>
Equipment	Location
Spill control pads	Hickey 174 (Bio)
	Hickey 254, 257 (Chem)
Acid/base neutralizer	Hickey 174, 181, 184 (Bio)
Vapor blanket sheets	Hickey 254, 257 (Chem)
Vermiculite	Hickey 257 (Chem)

<u>Mercury spills</u>

Metallic mercury is toxic by skin absorption, inhalation and ingestion. Long term exposure to low concentrations of vapor is harmful. Particular care should be taken in cleaning up mercury spills to ensure that the area is totally decontaminated. For cleaning up small spills of mercury (e.g., broken thermometers), follow the procedure given below. In the event of a large mercury spill, call Security.

- 1. Provide maximum ventilation in the contaminated area.
- 2. If the mercury is spilled in an oven or other heated device, turn off the unit, evacuate the laboratory and call Security.
- 3. Avoid contamination of shoes or other items in the area.
- 4. Never sweep with a broom, as this breaks up the droplets and results in increased vaporization.
- 5. Push pools of mercury together.
- 6. Pick up the pools with a medicine dropper, mercury pump, or pipette with a closed bulb and transfer into a plastic bottle.
- 7. Use mercury clean-up powder to form an amalgam of the residual that can then be picked up.
- 8. All mercury and clean-up debris must be disposed of as hazardous waste as described in Chapter 9.

Chapter 15: Exposure Evaluation and Medical Consultation

Chemical exposure monitoring is conducted by the EHS Office when there is reason to believe that exposure levels routinely exceed the OSHA established action level or permissible exposure limit for a specific chemical. Employees with concerns regarding their exposure should contact the EHS Office. In the event of an exposure incident or when a student or employee experiences symptoms of exposure, the EHS Office should be contacted immediately.

Providence College will provide medical consultations for employees under any of the following circumstances:

- 1. When an employee develops symptoms of exposure.
- 2. When chemical exposure monitoring reveals that routine exposures are above the OSHA established action levels or permissible exposure limit and medical surveillance requirements have been established by OSHA for the specific chemical.
- 3. When an event, such as a spill, results in the likelihood of hazardous exposure.

Medical consultation services will be provided by a health care provider chosen by Providence College. Employees requesting medical consultation should contact the EHS Office.

Chapter 16: Nuclear Magnetic Resonance Spectrometer Safety Program

Student access to the nuclear magnetic resonance (NMR) spectrometer laboratory shall be under the supervision of a NMR-trained chemistry or biochemistry professor.

All users shall work cautiously around the high-field magnets. Failure to do so can result in costly instrument damage and serious personal injuries including death. Students must understand the hazards present and follow all safety practices when using the NMR. Students will read the following NMR safety information and sign the Student NMR Safety Agreement in Appendix K prior to using the NMR laboratory located in Albertus Magnus 316 A.

A. High magnetic fields

High-field NMR instruments use powerful superconducting magnets to generate magnetic fields. Superconducting magnets use liquid helium and nitrogen as cryogens to keep the magnet core at a very low temperature. Both of these cryogens must be periodically replenished as both slowly boil off.

REMEMBER: The magnet is always on!

NMR magnets have very strong static magnetic fields. Magnet strength is normally described in terms of gauss (G) or tesla (T) units. (1 T = 10,000 G). Providence College has one NMR magnet located in Albertus Magnus:

Albertus 316 A 400 MHz = 9.4 Tesla, 94,000 Gauss

The strength listed above is the strength of the field at the magnet's core (inside the bore where the sample is placed). To put this in perspective, the center of the NMR magnet is 9.4 times stronger than the electromagnets used to move old cars around at a junkyard (~ 1 T) and several hundred times stronger than the Earth's magnetic field (30-70 μ T). The strength of the magnetic field falls off dramatically as you move away from the magnet's core. The degree to which it decreases depends on the physical size and geometry of the magnet. Human bodies are not magnetic, so we cannot directly feel the strength of the magnetic field. For most purposes, you only need to know the location where the magnetic field strength drops to 5 Gauss and below.

B. Gauss Line Safety

Signs, plastic chains, and/or marks on the floor mark the location of the 5 Gauss field line around each NMR magnet. The magnetic field inside the 5 Gauss region can cause damage to medical implants and pacemakers.

DO NOT ENTER THE 5 GAUSS REGION IF YOU HAVE A PACEMAKER OR ANY MEDICAL IMPLANT THAT IS SUSCEPTIBLE TO A STRONG MAGNETIC FIELD!

Before entering the 5 Gauss region remove all metal objects, including but not limited to cell phones, jewelry, watches, paperclips, credit or any magnetic strip cards, or any other metal clothing or accessory.

The location of the 10 Gauss region is located slightly inside the 5 Gauss region. At this field strength, watches, credit cards, and other personal items can be damaged. More importantly, keep all tools and equipment outside this area.

Assume all metal objects are ferromagnetic and will be attracted to the magnet. Metal objects can be attracted to the magnet causing flying metal projectiles. Ferromagnetic objects can reach speeds approaching 45 mph entering the bore of the magnet. These objects can cause personal injury or death if there is anyone between them and the center of the magnet. If the objects strike the magnet they can distort the magnet's wires or internal dewars and/or become lodged inside the magnet bore. This can cause the magnet to quench.

C. Magnet Quench

A quench is caused when the magnet is damaged or the equilibrium inside the magnet coil is disturbed. This causes the magnet to lose its magnetic field and can damage the superconducting coils inside. The loss of superconductivity and the development of resistance in the magnetic coil results in the generation of heat and a rapid vaporization of the liquid helium and liquid nitrogen.

Due to their large expansion ratios (nitrogen 695:1, helium 760:1), these gases can quickly displace all the oxygen in the NMR room and may cause asphyxiation.

A QUENCH IS VERY DANGEROUS SINCE THE RAPIDLY EXPANDING GASES WILL DISPLACE ALL THE AIR (OXYGEN) IN THE ROOM. IF A MAGNET APPEARS TO BE IN ANY DANGER OF QUENCHING - LEAVE THE AREA IMMEDIATELY AND CLOSE THE DOOR BEHIND YOU AS YOU EXIT.

IMMEDIATELY NOTIFY THE EMERGENCY CONTACTS LOCATED ON THE EXTERIOR DOOR.

D. Cryogenic Gases and Ventilation

Nitrogen and helium are both odorless, colorless, and nontoxic. However, in a gaseous state both gases will displace oxygen presenting a potential oxygen-deprived environment. Sudden discharge of these gases from the system, such as in a quench, may result in suffocation if

adequate ventilation is not available. The NMR lab is equipped with an automatic emergency ventilation system. In the event that the magnet quenches, oxygen sensors located near the ceiling and the floor will trigger the alarm and the emergency ventilation system will be activated. This system will evacuate the gases from the room. When the emergency ventilation system is activated, a blue light above the exterior side of the door will illuminate. If the blue light is on do not enter the room, call the emergency contacts listed on the exterior door.

In the event that it is necessary to manually activate the emergency ventilation system, push the RED BUTTON to the right of the door as you exit the NMR lab. This is labeled Emergency Ventilation. There is also a red Emergency Ventilation button located outside the NMR lab to the left of the door.

E. Personal Protective Equipment

Personal protective equipment, as defined in chapter 4, is mandatory.

F. Magnet Filling Operation

The liquid helium and liquid nitrogen used in the NMR magnets are extremely cold. Helium liquefies at 4 K (-269°C), and nitrogen liquefies at 77 K (-196°C). Prolonged contact with liquid nitrogen or even brief contact with liquid helium will cause frostbite.

Section 2: Chemical Hazards

The chapters within Section 2 provide guidelines for the safe handling of "hazardous chemicals." The OSHA Laboratory Standard defines a "hazardous chemical" as one which exhibits physical or health hazards as follows.

"Physical Hazard" - a chemical for which there is scientifically valid evidence that it is a combustible liquid, a compressed gas, explosive, flammable, an organic peroxide, an oxidizer, pyrophoric, unstable (reactive) or water reactive.

"Health Hazard" - a chemical for which there is statistically significant evidence based on at least one study conducted in accordance with established scientific principles that acute or chronic health effects may occur...includes...carcinogens, toxic or highly toxic agents, reproductive toxins, irritants, corrosives, sensitizers, hepatotoxins, nephrotoxins, neurotoxins, agents which act on the hematopoietic (blood) system, and agents which damage the lung, skin, eyes, or mucous membranes.

The terms "chemical," "substance," and "material" are used interchangeably with "hazardous chemical," "hazardous substance," and "hazardous material" throughout the Chemical Hygiene Plan. All refer to those chemicals defined as hazardous by OSHA as described above. The requirements outlined in the chapters of Section 2 apply to the laboratory use of substances that could result in chemical exposure under routine or emergency situations. They do not apply to the use of chemicals when no exposure is possible. For example, the use of lead shielding for radiation protection does not result in lead exposure and, consequently, the requirements for handling lead as a reproductive toxin in Chapter 22 do not apply.

The attitude of those working in the laboratory is the most important factor in the safe conduct of laboratory experiments. All stages of an experiment, from design through completion, must consider safety as a guiding principle. The key to designing and carrying out safe laboratory experiments is knowledge of the potential hazards. It is the responsibility of each individual working in the laboratory to become thoroughly familiar with the hazards of the substances he/she is using and operations he/she is performing.

Chapter 17: Flammables

The Globally Harmonized System of Classification and Labelling of Chemicals (GHS) defines a flammable liquid as one with a flash point less than $60^{\circ}C(140^{\circ}F)$, and a combustible liquid as one with a flash point between $60^{\circ}C(140^{\circ}F)$ and $93^{\circ}C(200^{\circ}F)$.

GHS Category	Signal Word/Pictogram	Hazard Statement	Criteria
Category 1	DANGER	Extremely flammable liquid and vapor	Flash point < 23°C and initial boiling point ≤ 35°C
Category 2	DANGER	Highly flammable liquid and vapor	Flash point < 23°C and initial boiling point > 35°C
Category 3	WARNING	Flammable liquid and vapor	23°C < Flash point < 60°C
Category 4	None	Combustible liquid	60°C < Flash point < 93°C

Table 17.1: GHS classification of flammable and combustible liquids

A. Storage and Dispensing

Bulk dispensing of flammable liquids

All dispensing from bulk containers (5 - 55 gallon containers) of Category 1 or 2 flammable liquids must be done in the central storage area. The Chemical Hygiene Officer trains those authorized to dispense flammable liquids and keeps a list of those authorized on file.

These solvents can only be dispensed into approved (Underwriters Lab or Factory Mutual) flammable safety cans equipped with spring loaded covers and flame arresters, except when glass is necessary to avoid contamination. Drums must be grounded and the container bonded (connection between the drum and safety can) to prevent accumulation of static electricity. Drums must be equipped with a self-closing faucet or pump approved for flammable dispensing.

Laboratory and prep room storage

The quantity of flammable liquids, solids, and gases stored in laboratories should be kept at a minimum. If chemicals are purchased in large lots for future use, containers should be stored in the central storage area until needed. Category 1 or 2 flammables in containers larger than 4 liter/1 gallon must be stored in the central storage area or the synthetic Chemistry research storeroom.

The NFPA limits the total quantity of flammable liquids, according to class, that can be stored in a laboratory based on its square footage (Table 17.2, column 3). These limits are based on the NFPA's classification of flammable liquids, shown in Table 17.3.

Table 17.2: NFPA flammable liquid storage limits

NFPA Combustible Liquid Class	Max Qty/100 ft², In Use ª	Max Qty/100 ft², Total ^b
Ι	2 gal	4 gal
I, II, IIIA	4 gal	8 gal

a "In Use" means all flammable and combustible liquids in the lab, stored outside safety cabinets or cans.
b "Total" means all flammable and combustible liquids in the lab, including what is stored in safety cabinets or cans.
(National Fire Protection Association, 2015)

The preferred storage method within laboratories is in flammable storage cabinets meeting NFPA standards for liquids or solvents, in UL or FM approved flammable safety cans, or in flammable refrigerators or freezers meeting NFPA Standards. Storage in flammable cabinets should not exceed the rated capacity of the cabinet.

The NFPA also limits the quantity of "in use" flammable liquids, those not stored in flammable cabinets and safety cans (Table 17.2, column 2).

Classes of Flammable and Combustible Liquids			
Class	Boiling Point °C(°F)	Flash Point °C(°F)	Examples
Flammable IA	<37.8 (100)	<22.8 (73)	ethyl ether, pentane
Flammable IB	<u>≥</u> 37.8 (100)	<22.8 (73)	acetone, ethyl alcohol
Flammable IC	-	22.8 (73) ≤ and <37.8 (100)	butanol, isoamyl acetate
Combustible II	-	37.8 (100) <u><</u> and <60 (140)	formalin, cyclohexanone

Table 17.3: NFPA classes of flammable and combustible liquids

Combustible IIIA	-	60 (140) <u><</u> and <93.3 (200)	phenol, dichlorobenzene
Combustible IIIB	-	<u>≥</u> 93.3(200)	ethylene glycol, mineral oil

(National Fire Protection Association, 2015)

Flammable materials refrigerators and freezers have spark-free interiors. Explosion-proof units also have spark-free exteriors and are designed for use in hazardous environments. All units designed for flammable storage, meeting NFPA Standards, should be clearly marked as "approved for flammable storage". All units not approved should be clearly marked "not for flammable storage" or other similar wording.

The NFPA requirements in Table 17.2 also apply to prep rooms.

B. Laboratory Use

All laboratory procedures using flammable substances should be designed to

- minimize the release of flammable vapors,
- prevent the travel or accumulation of vapors,
- eliminate sources of ignition, and
- minimize the amount of flammable substances or other combustible materials (e.g., paper) in the vicinity of the handling area.

The following precautions should always be followed. These precautions do not apply to the use of natural gas as a fuel for combustion. Additional precautions may be necessary in certain situations. Substances with a flash point above 100°F may be handled as non-flammable unless the substance is heated. The Chemical Hygiene Officer can assist in evaluating the hazards of particular operations or experiments if needed.

- 1. Volatile flammable substances should always be tightly sealed when not in use, and should only be opened and used in a fume hood.
- 2. Use flammable liquids in fume hoods whenever possible, particularly when transferring large quantities or heating in open containers.
- 3. Always use flammable gases in a fume hood.
- 4. Never use open flames in close proximity to flammable chemicals or combustible materials.
- 5. Control other sources of ignition and heat in the laboratory such as electric motors and ovens in areas where flammable vapors are expected to exceed 10% of the lower flammability limit.
- 6. Use non-sparking equipment and control static electricity.
- 7. Use steam baths, heating baths, or explosion-proof heating equipment for heating.
- 8. When transferring flammable liquids in metal containers, ground and bond the containers.

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- 9. Minimize the generation of dust when handling flammable solids.
- 10. Flame resistant lab coats (NOMEX or FR-treated cotton) should be worn when working with >1L of GHS category 1 or 2 flammable liquids (GHS Hazard Warnings H224 and H225). In addition, non-synthetic clothing (including long pants; no skin exposed below the waist; shoes that cover the entire foot) should be worn.

Chapter 18: Reactives

The GHS indicates the hazards of reactive materials as shown in Table 18.1. Table 18.1: GHS reactive materials hazards

Hazard type	Pictogram	Category/ Type	Hazard statement
Flammable gases / chemically unstable gases		Category A	May react explosively even in the absence of air
Flammable Solids		Category 1	Flammable Solid
Pyrophoric Liquids		Category 1	Catches fire spontaneously if exposed to air
Pyrophoric Solids		Category 1	Catches fire spontaneously if exposed to air
Self-Heating Substances and Mixtures		Category 1	Self-heating; may catch fire
In contact with water emit flammable gases		Category 1	In contact with water releases flammable gases which may ignite spontaneously
Self-Reactive Substances and Mixtures		Туре А	Heating may cause an explosion
Self-Reactive Substances and Mixtures		Туре В	Heating may cause a fire and explosion
Organic Peroxides		Туре А	Heating may cause an explosion
Organic Peroxides		Туре В	Heating may cause a fire or explosion
Explosives	$\mathbf{\wedge}$	GHS Division 1.1	Mass Explosion Hazard
Explosives		GHS Division 1.2	Projection Hazard
Explosives		GHS Division 1.3	Fire hazard, minor blast hazard or minor projection hazard
Oxidizing Solids and Liquids	(Category 1	May cause fire or explosion; strong oxidizer

A. Reactive Hazards

Reactive substances can, under certain conditions, release very large and potentially dangerous amounts of energy. They can lead to reactions that differ from the routine mainly in the rate at which they progress. A chemical reaction can be considered routine if the reaction rate is relatively slow or can be easily controlled.

Spontaneous decomposition or changes in physical state, even at a slow rate, may create a reactive hazard by producing a less stable compound. For some substances, this decomposition is rapid and violent. For others it is so slow as to be imperceptible but results in a byproduct with a much higher reactivity hazard. Peroxides that can form when certain organic compounds are exposed to air radically increase the hazards of working with those compounds. The formation of shock sensitive picric acid crystals from an aqueous solution is a serious hazard created by a simple physical state change in the same compound.

Water reactives

Water reactive materials are those that react violently with water. They can develop pressure; generate flammable, explosive, corrosive, or toxic gases; or ignite or explode when exposed to water or moisture. Examples include the following:

alkali and alkaline-earth metals (sodium, lithium, calcium, potassium, magnesium) aluminum chloride anhydrous metal halides (aluminum tribromide, germanium tetrachloride) anhydrous metal oxides (calcium oxide) benzoyl chloride calcium carbide calcium oxide nonmetal halides (boron tribromide, phosphorous pentachloride) nonmetal halide oxides (inorganic acid halides, phosphoryl chloride, sulfuryl chloride, chlorosulfonic acid) nonmetal oxides (acid anhydrides, trioxide) tert-butyl lithium and some other organometallic compounds

Pyrophorics

Pyrophoric substances are gases, liquids, and solids that have the potential to spontaneously ignite in air, without the influence of heat or ignition sources. Pyrophoric substances can develop pressure, generate flammable or explosive gases, ignite or explode when exposed to air. They often have corrosive, water reactive, and peroxide forming properties. Improper use of these materials has resulted in fires, damage to lab equipment, injury and even death. Examples include the following:

alkylmetal derivatives (ethoxydiethylaluminum and dimethylbismuth chloride) analogous derivatives of nonmetals including diborane, dimethylphosphine, triethylarsine, dichloro(methyl)silane carbonylmetals (pentacarbonyliron and octacarbonyldicobalt) finely divided metals (calcium, titanium) metal hydrides (potassium hydride and germane) organometallic compounds (sec-butyl lithium, tert-butyl lithium) partially or fully alkylated metal hydrides (diethylaluminum hydride, triethylbismuth) sodium methoxide triethylaluminum white phosphorus

Incompatible chemicals

Accidental contact of incompatible substances can result in a serious explosion or the formation of substances that are highly toxic or flammable or both. Because the magnitude of risk depends on quantities, chemical incompatibilities will not usually pose much, if any, risk if the quantity of the substance is small.

B. Explosive Hazards

An explosive is any chemical compound that, when subjected to heat, impact, friction, detonation, or other initiation, undergoes a rapid chemical change. Highly explosive materials require very little initiating force. Explosions release large volumes of gases that exert pressure on the surroundings. Heat, light, mechanical shock, and certain catalysts can initiate explosive reactions.

Some substances require very little energy of activation to initiate a spontaneous reaction. Some are set off by the action of a metal spatula on the solid; some are so sensitive that they are set off by the action of their own crystal formation. If the reaction is exothermic, the energy initially produced may accelerate a continued reaction and a release of energy too violent to be controlled. Temperature, shock, static electricity, or light may trigger an uncontrollable reaction. In some combinations, one compound will act as a catalyst reducing the amount of energy normally needed to initiate or sustain a reaction.

<u>Oxidizers</u>

Oxidizers are materials that can readily remove electrons from a substance. In a second sense, an oxidizer is a chemical species that transfers electronegative atoms, usually oxygen, to a substance. When contaminated with organic materials, (e.g., wood. paper, organic chemicals), or other easily oxidizable materials (e.g., metal powders), oxidizers can form unstable and explosive compounds sensitive to shock. Examples include the following:

bromine and compounds chlorine and compounds chromates and dichromates chromium trioxide chromic acid fluorine iodine and compounds manganese dioxide nitrates nitric acid nitrites nitrogen trioxide permanganates peroxides persulfates phosphomolybdic acid picrates sodium bismuthate sulfuric acid

Temperature-sensitive substances

Temperature sensitive substances may decompose when held above their maximum safe storage temperature resulting in pressure buildup, flammable or explosive gas generation, ignition, or explosion. Examples include the following:

certain oxidizers (perchlorates, chlorates, nitrates, bromates, chlorites, iodates) certain "azo" compounds lithium nitrate organic peroxides phenylhydrazine hydrochloride

Spontaneous decomposition

Compounds which change structure over time and with no apparent stimulation may develop pressure, generate flammable or explosive gases, ignite, or explode. Examples include the following:

benzoyl peroxide (dry) contaminated concentrated hydrogen peroxide nitroglycerine

Shock, friction, and static discharge-sensitive substances

Compounds that are sensitive to shock, friction, and static discharge may violently decompose when initiated. Examples include the following:

acetylides	nitro compounds
azides	nitroso compounds
contaminated oxidizers	organic nitrates
diazo compounds	organic and inorganic peroxides (see below)
explosives	ozonides
fulminates	perchlorate salts
halamine	picric acid (trinitrophenol)

Reactive under special conditions

Certain compounds pose a serious risk of violent reaction under certain specific conditions. Examples include the following:

ammonia carbon sulfide chromium trioxide-pyridine complex diethyl, diisopropyl, and other ethers (tetrahydrofuran (THF), 1,4-dioxane, branched chain ethers) dimethyl sulfoxide (DMSO) halogenated compounds (chloroform, carbon tetrachloride) hydrogen peroxide liquid nitrogen open to the atmosphere lithium aluminium hydride ozone permanganates phosphorus phosphorous trichloride sodium amide trichloroethylene

Peroxides and peroxidizable compounds

Many common laboratory compounds can form peroxides when exposed to air over a period of time. A single opening of a container to remove some of the contents can introduce enough air for peroxide formation to occur. Over time, some compounds continue to build peroxides to potentially dangerous levels, whereas others accumulate a relatively low equilibrium concentration of peroxide, which becomes dangerous only after being concentrated by evaporation or distillation. The peroxide becomes concentrated because it is less volatile than the parent compound. Peroxides are sensitive to heat, friction, impact, and light and are among the most hazardous substances that are encountered in laboratories. Their hazard potential is all the greater because they may not be suspected or detected in commonly used solvents or reagents. Many explosions have occurred during distillation of peroxide-containing substances particularly when the distillation has been taken to or near to dryness.

Crystal formation or cloudy appearance inside a container is a possible sign of peroxide formation. Crystal formation is most likely (and most hazardous) around the cap. Friction caused just by turning the cap can cause an explosion that ignites flammable solvent in the container.

Peroxide formation can also occur in many polymerizable, unsaturated compounds. These peroxides can initiate an uncontrolled, and sometimes explosive, polymerization reaction.

Structural groups of chemicals that can form peroxides, listed in approximate order of decreasing hazard, include:

18: Reactives

Organic compounds:

ethers and acetals with alpha hydrogen atoms olefins with allylic hydrogen atoms chloroolefins and fluoroolefins vinyl halides, esters, and ethers dienes vinylacetylenes with alpha hydrogen atoms alkylacetylenes with alpha hydrogen atoms alkylarenes that contain tertiary hydrogen atoms alkanes and cycloalkanes that contain tertiary hydrogen atoms acrylates and methacrylates secondary alcohols ketones that contain alpha hydrogen atoms aldehydes ureas, amides, and lactams that have a hydrogen atom on a carbon atom attached to nitrogen.

Inorganic compounds:

alkali metals, especially potassium, rubidium, and cesium metal amides organometallic compounds with a metal atom bonded to carbon metal alkoxides

Explosive boiling

Extreme differences in physical state can cause an uncontrollable release of energy. For example, bringing a hot liquid, such as an oil, into contact with a liquid with a lower boiling point such as water will cause instantaneous vaporization of the lower boiling point liquid and a violent release of energy. Even if the material does not explode directly, the sudden formation of explosive or flammable vapor can be very dangerous.

C. Storing Highly Reactive Substances

The following storage guidelines are from Prudent Practices in the Laboratory: ³

- Do not open a container of highly reactive material that is past its expiration date. Call the EHS Office for special instructions.
- Do not open a liquid organic peroxide or peroxide former if crystals or a precipitate are present. Call the EHS Office for special instructions.
- For each highly reactive chemical, determine a review date to reevaluate its need and condition and to dispose of (or recycle) material that degrades over time.

³ National Research Council, 2011. *Prudent Practices in the Laboratory: Handling and Management of Chemical Hazards*. National Academy Press.

- Segregate the following materials: oxidizing agents from reducing agents and combustibles, powerful reducing agents from readily reducible substrates, pyrophoric compounds from flammables, and perchloric acid from reducing agents.
- Store highly reactive liquids in trays large enough to hold the contents of the bottles.
- Store perchloric acid bottles in glass or ceramic trays.
- Store peroxidizable materials away from heat and light.
- Store materials that react vigorously with water away from possible contact with water, and not under sinks.
- Store thermally unstable materials in a refrigerator. Use a refrigerator with these safety features:
 - o all spark-producing controls on the outside,
 - a magnetically locked door,
 - $_{\circ}$ an alarm to warn when the temperature is too high, and
 - a backup power supply.
- Store liquid organic peroxides at the lowest possible temperature consistent with the solubility or freezing point. Liquid peroxides are particularly sensitive during phase changes. Follow the manufacturer's guidelines for storage of these highly hazardous materials.
- Store particularly sensitive materials or larger amounts of explosive materials in explosion relief boxes.

The GHS includes information for preventing chemical exposure and accidents. "P Statements" are provided which are precautionary measures. SDSs should be consulted for the full text of these statements, and these measures are to be followed.

D. General Safety Procedures for Working with Reactive Chemicals

The following general guidelines should be followed when working with reactive materials. Additional measures may be necessary depending on the specific materials and/or specific procedures used.

- 1. Find out as much as possible about the reagents and procedures before the experiment.
- 2. Investigate the purity of the materials. Determine whether impurities or spontaneous decomposition products (such as peroxides) will make the experiment more hazardous.
- 3. Conduct small scale preliminary experiments or rely on published research, if available, to assess the thermodynamic and physical properties of the reaction.
- 4. Use as little of the substance or as dilute a solution as possible.
- 5. Consider all methods of controlling reaction variables. The rate of addition can be controlled as well as the rate at which the energy of activation is supplied. Cool exothermic reactions adequately to control the reaction rate. Remember to provide cooling arrangements for both liquid and vapor stages if appropriate. Pressure relief valves should be included in pressurized systems and checked before adding chemicals to the system.

- 6. Determine the proper degree of agitation and mixing rate. Add oxidants slowly with appropriate cooling or mixing.
- 7. Use a face shield in addition to goggles when appropriate.
- 8. When working with pyrophorics and explosives, NOMEX 3A flame-resistant lab coats are required to be worn. In addition, non-synthetic clothing (including long pants; no skin exposed below the waist; shoes that cover the entire foot) should be worn.
- 9. Work in a fume hood using the sash as a protective shield.
- 10. Have emergency equipment at hand. Be certain that you know where the nearest fire extinguisher is and that it is appropriate for the type of potential fire hazard (see Chapter 5, for classes of fire extinguishers). It is important to consider not only which type of extinguisher would be most effective but also if a particular type of extinguishing medium would cause an increased hazard. For example, diborane, pentaborane, and diethyl zinc react violently with halogenated extinguishing agents.
- 11. Notify people in the laboratory of any new or unique hazards that could potentially be created by use of a reactive substance.

E. Standard Operating Procedures

If a student will be using a reactive chemical, with the exception of oxidizer solutions used in teaching laboratories, the faculty member must develop a written Standard Operating Procedure (SOP). Principle investigators and laboratory supervisors will use the SOP to train students in the use of the reactive material, and that training will be documented as described in Chapter 6.

Since the definition of a reactive substance is broad, it may be difficult to decide what needs an SOP and what does not. As a rule of thumb, an SOP is necessary when working with any substance that poses a serious risk to human health under the conditions that it is being used. For example, dimethyl sulfoxide (DMSO) reacts violently with a wide variety of active halogen compounds, such as acyl chlorides and active metal hydrides. So, the use of DMSO with these substances should have an SOP.

Before working with any substance that bears any of the hazard pictograms in Table 18.1 or is listed in the examples in sections A and B of this chapter, each faculty or supervising staff member should investigate if there is a risk of a harmful reaction based on the conditions of use. If that is the case, an SOP is necessary before working with it.

F. Special Procedures for Peroxide Forming Chemicals

It is important that information on the age of peroxide forming compounds be maintained and that these compounds be tested or disposed of on a regular basis. Peroxidizable compounds should be labeled upon receipt with the preprinted label shown in Figure 18.1.

Figure 18.1: Peroxidizable compound label



Some peroxide formers should be tested more frequently than the 12 months specified on the labels. The label should be modified by hand in such cases. These labels should also be placed on any other compounds known to be peroxide formers. Upon opening the container for the first time, the date should be filled in and the discard period adjusted if necessary. Peroxide test strips that are available from the central storage area.

The following are recommendations for testing or disposal of potential peroxide forming chemicals. All chemicals on these lists should be labeled with the label shown in Figure 18.1.

Group A - Chemicals that form explosive levels of peroxides without concentration

(Safe storage time after opening - 3 months)

1,1- Dichloroethylene	75-35-4 (Vinylidene chloride)
2-Chloro-1,3-Butadiene	126-99-8 (Chloroprene)
Butadiene	106-99-0
Divinyl acetylene	821-08-9
lsopropyl Ether	108-20-3
Tetrafluoroethylene	116-14-3
Vinyl Ether	109-93-3 (Divynyl ether)

Group B – Chemicals that form explosive levels of peroxides on concentration

(Safe storage time after opening - 12 months)

2-Butanol	78-92-2
2-Cyclohexan-1-ol	822-67-3
2- Hexanol	626-93-7
2-Pentanol	6032-29-7
3-Methyl-1-Butanol	123-51-3 (Isoamyl Alcohol)
4-Heptanol	589-55-9
4-Methyl-2-Pentanol	108-11-2
Acetal	105-57-7
Acetaldehyde	75-07-0
Alpha-Methyl-Benzyl Alcohol	98-85-1 (Phenyl Ethanol)
Benzyl Alcohol	100-51-6

Cyclohexanol	108-93-0
Cyclohexene	110-83-8
Cyclooctene	931-87-3
Cyclopentene	42-29-0
Decahydronaphthalene	91-17-8
Diacetylene	460-12-8
Dicyclopentadiene	77-73-6
Dioxane	123-91-1 (1,4 Dioxane)
Ethylene Glycol Dimethyl Ether	110-71-4 (1,2 Dimethoxyethane; Monoglyme)
Ethyl Ether	60-29-7 (Diethyl Ether)
Furan	100-00-9
Isopropyl Benzene	98-82-8 (Cumene)
Methylcyclopentane	96-37-7
Methyl Isobutyl Ketone	108-10-1(4-Methyl-2-pentanone; Hexone)
Penten-1-ol	821-09-0
Propyne	74-99-7 (Methyl Acetylene)
Tetrahydrofuran	109-99-9
Tetrahydronaphthalene	119-64-2
Other Secondary Alcohols	

Group C – Chemicals which may autopolymerize as a result of peroxide accumulation

(Safe storage time after opening: inhibited chemicals -12 months; uninhibited chemicals -24 hours) Note: Do not store inhibited chemicals in this group under inert atmospheres

1,1-Dichloroethylene	75-35-4 (Vinylidene Chloride)
2-Chloro-1,3-Butadiene	126-99-8 (Chloroprene)
Acrylic Acid	79-10-7
Acrylonitrile	107-13-1
Buten-3-yne	689-97-4 (Vinyl acetylene + Butenyne)
Chlorotrifluorethylene	79-38-9
Methyl Methactrylate	80-62-6
Phenethyl Alcohol	60-12-8 (Phenyl Ethanol)
Styrene	100-42-5
Tetrafluoroethylene	116-14-3
Vinyl acetate	108-05-4
Vinyl chloride	75-01-4 (Monochloroethylene)

Source: Ernest Orlando Lawrence Berkley National Laboratory, Chemical Hygiene and Safety Plan, 2001.

Chapter 19: Compressed Gases

A. Defining Compressed Gases

Compressed gas cylinders are defined by the U. S. Department of Transportation (DOT) as any materials or mixtures in containers having an absolute pressure in excess of 40 psi at 20°C (70°F) or in excess of 104 psi at 54.5°C (130°F).

Compressed gas cylinders should be considered high-energy sources regardless of the type of gas and all should be treated as potential explosives. Compressed gases have many properties that make them a unique hazard such as their pressure, diffusivity, low flash points for flammable gases, low boiling points, and, for some, no visual and/or odor warnings.

The following are general safety precautions for working with compressed gases.

B. Cylinder Storage

Delivery area storage

Large cylinders are stored in the cylinder storage area until they are needed in the laboratory, as are all empty cylinders. Storage of cylinders outside of the cylinder storage area is prohibited.

General storage requirements

- 1. Store oxygen away from flammable gases. While in the cylinder storage area, oxygen and fuel gases must be separated by a distance of at least 25 feet or by a 5-foot high noncombustible wall. This requirement does not apply to cylinders in use.
- 2. The valve protection cap must be kept on at all times, except when a cylinder is in use.
- 3. Cylinders must be chained or strapped in place to prevent them from falling over.
- 4. Cylinders of corrosive gases should be stored for the shortest possible time period: under three months is preferable. Lecture bottles may be kept for longer periods of time. All cylinder components are to be inspected before and after the use of corrosive gases.

Lecture bottle storage

Lecture bottle size cylinders pose the same hazards as larger cylinders, and storage should comply with the standards listed above for General Storage Requirements, with the exception that lecture bottles may be stored securely on their sides or clamped to a ring stand.
C. Inspection of Cylinders

Before using cylinders, they should be inspected to ensure they show no signs of damage or corrosion. Also, they should have:

- a valve protection cap
- a DOT or ICC label
- the date of the last hydrostatic test (usually stamped on the cylinder just below the serial number)⁴
- labels or stenciling identifying the contents (color coding is not acceptable as a contents label because there is no universal color code for identifying gas cylinders)
- identity of the manufacturer

D. Moving Cylinders

Faculty members, staff, or trained students can move cylinders from the cylinder storage area to the laboratory.

- 1. Before moving cylinders, make sure that:
 - a. the valve protection cap is on, and
 - b. the destination is equipped with cylinder securements.
- 2. Always consider cylinders full and handle them accordingly; the same hazards exist even if the cylinder is only partially full.
- 3. Use a hand truck to transport cylinders. Do not drag, roll, or slide cylinders.
- 4. The valve protection cap should remain on until the cylinder has been secured in its final position and is ready for use.
- 5. Never drop a cylinder or permit cylinders to strike each other violently.
- 6. Protect cylinders from any object that will produce a cut or abrasion in the surface of the metal.
- 7. Mount cylinders so that the valve is easily accessible and the label is readable.
- 8. Always chain or strap cylinders immediately. Cylinders must be secured individually. Do not leave a cylinder in a laboratory if equipment is not available to secure it.

E. Laboratory Use

 Attach the proper regulator designed for the particular gas that is being used. Cylinder valves have been standardized for specific families of gases to prevent the interchange of regulator equipment between gases that are not compatible. Do not force the fitting of a regulator to a cylinder. Be sure that all components of a distribution system are

⁴ Most cylinders must be tested every five years. Cylinders that only require testing every ten years have a fivepointed star stamped next to the date.

compatible with the gas in use. Corrosive gases require special attention to the materials in the distribution system.

- 2. After connecting the regulator, secure all hose connections with clamps, secure any loose hoses to prevent sudden movement when pressure is supplied, and place a trap between the regulator and the reaction vessel.
- 3. Bond and ground all cylinders and piping containing flammable gases to prevent the hazards caused by the buildup of static electricity.
- 4. Start the gas flow with the following procedure.
 - a. With the regulator secured to the cylinder valve outlet, turn the delivery pressure adjusting screw counterclockwise until it turns freely.
 - b. Next, slowly open the cylinder valve until the cylinder pressure gauge on the regulator reads the cylinder pressure. The cylinder valve should be opened by hand; never use a wrench or other tool unless the vendor supplies a special tool for that purpose.
 - c. With the cylinder valve open and the flow control valve (the outlet from the regulator) in closed position, set the desired delivery pressure by turning the delivery-pressure adjusting screw clockwise until the desired pressure is reached.
 - d. Flow from the cylinder can now be commenced by opening the flow control valve at the outlet of the regulator.
- 5. Door signs should be posted in rooms in which flammable compressed gases are present.
- 6. Never mix gases in a cylinder, unless it is a specially designed cylinder such as for calibration gases.
- 7. Never completely empty a cylinder. Leave a slight pressure (about 25 pounds) to keep out contaminants that may react with the contents or corrode the cylinder.

F. Special Precautions

<u>Acetylene</u>

- 1. Gaseous acetylene under pressure may decompose with explosive force, and should not be used at pressures in excess of 15 psig (30 psi absolute pressure). Acetylene pressure gauges should have a warning red line at this point.
- 2. Acetylene in cylinders is dissolved in a liquid (e.g., acetone) and should always be used in an upright position. Do not use a cylinder that has been stored or handled in a non-upright position until it has remained in an upright position for at least 30 minutes.
- 3. The outlet line of an acetylene cylinder must be protected by a flash arrester.
- 4. Use the correct kind of tubing to transport the gaseous acetylene. Some tubing materials, such as copper, form explosive acetylides.

<u>Oxidizers</u>

Oxidizers under pressure (oxygen, chlorine, etc.) will rapidly oxidize organic material, such as oil or grease, resulting in an explosion. Never use oil or grease on valves or gauges intended for oxygen cylinders.

Chapter 20: Cryogens

A. Cryogenic Systems

Cryogenic systems are devices for creating or maintaining very low temperatures, below -73.3°C (-100°F). Temperatures in the cryogenic range are generally obtained by liquefying or solidifying gases (cryogens).

The most commonly used cryogens and their properties are listed in Table 20.1 below.

Cryogenic Gas	Normal Boiling Point (°C)	Flammable	Toxic	Odor
carbon dioxide	-78.5	No	Yes	Slightly Pungent
hydrogen	-252.7	Yes	No	No
nitrogen	-195.8	No	No	No
helium	-268.9	No	No	No
argon	-185.7	No	No	No
fluorine	-187.0	No	Yes	Sharp
oxygen	-183.0	No (Oxidizer)	No	No
methane	-161.4	Yes	No	No

Table 20.1: Properties of commonly used cryogens

(Furr, 1995)

The primary hazard of cryogenic materials is their extreme coldness that can result in frostbite and severe tissue damage. Accumulated vapors may also act as an asphyxiant. Liquid gases are extremely concentrated relative to room temperature gases and, consequently, their potential hazards are magnified. Liquefied inert gases, such as nitrogen, in contact with cold metal surfaces can cause condensation of oxygen from the room air resulting in an oxygen enriched atmosphere and, consequently, an increased fire hazard. The low temperatures involved also affect the properties of other materials, for example, rubber may become brittle and disintegrate and some metal alloys may become brittle.

Cryogens have very high liquid:vapor expansion ratios, for example, liquid nitrogen expands to 700 times its initial volume when it vaporizes. For hydrogen, 22 cubic feet of liquid can expand to 16,000 cubic feet of vapor. This expansion, if rapid enough or in a confined space, can cause a displacement of oxygen and consequently a life threatening asphyxiating atmosphere.

B. Storage and Handling Precautions

These are general precautions for handling cryogens. More specific safety guidelines should be established by the faculty or supervising staff member responsible for the use of a cryogen.

- 1. Store and use cryogens only in containers and equipment recommended for cryogenic service.
- 2. Avoid confined areas where vaporization occurs.
- 3. Ensure that all apparatus is properly vented to prevent accumulation of pressure and beware of the buildup of ice that could block vent lines.
- 4. Always wear chemical splash goggles, and a face shield in cases where there is a likelihood of contact.
- 5. Always wear long sleeves and/or a lab coat.
- 6. Watches, rings, or other jewelry that could trap the material next to the skin should not be worn.
- 7. If gloves are necessary to handle containers or cold metal parts, they should be impervious to the cryogen and loose enough to be thrown off in the case of contamination.
- 8. Liquid nitrogen, liquid air, or any other cryogen with a normal boiling point \leq -183°C should be used in such a way as to reduce the risk of condensing air, which can lead to an oxygen-rich, explosive environment.
- 9. Equipment must be kept clean to avoid contamination of organics with a cryogenic oxidant (e.g., liquid oxygen) or oxidants with cryogenic fuel (e.g., liquefied natural gas).
- 10. When flammable gases are being used, eliminate potential ignition sources.
- 11. Flammable and toxic gases should only be used in a fume hood.
- 12. If liquid nitrogen has a blue tint, it has been contaminated with oxygen and should be replaced. The contaminated material is dangerous and potentially explosive.
- 13. When spilled, liquid oxygen soaks into materials it comes into contact with, and the resulting mixture may be explosive.
- 14. Oxygen monitors shall be mounted in locations where cryogens are used on a regular basis.

Chapter 21: Corrosives

GHS uses the following hazard statements to warn of corrosivity to skin, eyes, and metals. These hazard statements are found on SDSs and manufacturer container labels of corrosive substances:

- H290 May be corrosive to metals
- H314 Causes severe skin burns and eye damage
- H318 Causes serious eye damage

A. Classes of Corrosive Chemicals

Corrosives are one of the most commonly encountered hazards in the laboratory. Corrosives are chemicals that can cause visible destruction of, or irreversible alteration in, living tissue, as well as destruction of other materials. The major classes of corrosive chemicals are strong acids and bases, dehydrating agents, and oxidizing agents. Some chemicals, such as sulfuric acid, belong to more than one class. In addition, many corrosives have other hazards such as reactivity (e.g., perchloric acid), flammability (e.g., organic acids), or toxicity (e.g., phenol).

The strength of acids and bases is defined as the degree of ionization of the acid or base in water. The inorganic or mineral acids, such as hydrochloric acid, a strong acid, generally ionize more than organic acids, such as acetic acid, a weak acid. Similarly, sodium hydroxide is highly ionized and is classified as a strong base, whereas ammonium hydroxide is slightly ionized and characterized as a weak base. The concentration of the acid or base, which is unrelated to its strength, refers to the percentage of the chemical dissolved in water. The corrosivity of acids and bases is dependent on their strength and concentration.

Dehydrating agents, such as sulfuric acid, sodium hydroxide, calcium oxide, and glacial acetic acid, are corrosive because of their strong affinity for water. This reaction with water is extremely exothermic. Because of this exothermic reaction with water, concentrated acids should always be added slowly to water. If water is added to the concentrated acid, the rapid generation of heat can cause the water to vaporize, causing the hot concentrated acid solution to splash.

Many oxidizing agents such as halogens, peroxides, nitric acid, and chromic acid are also corrosive, in additional to their fire and explosion hazard.

B. Hazards of Selected Corrosives

Corrosives can damage human tissue in their solid, liquid, and vapor states. Acute damage can be manifested as burns, ulceration, permanent tissue damage, or toxic effects. Many corrosives also have chronic hazards, as repeated exposure to even dilute solutions or vapors can

cause dermatitis, bronchitis, or eye damage. Acid burns are generally perceived as more painful that burns from other corrosives due to the formation of a protective protein layer that resists further penetration of the acid. In fact, tissue damage from bases is often more serious, as no protective layer is formed and the injury penetrates deeper. The destructive effect of corrosives is greatly increased when they are used at elevated temperatures.

In addition to their health hazards, many corrosives pose physical hazards as well. For example, many inorganic acids release flammable hydrogen gas when in contact with metals, posing a serious fire and explosion hazard.

The following are examples of some of the hazards of commonly used corrosives. The list is by no means exhaustive. The hazards of each corrosive should be thoroughly investigated prior to its use.

<u>Sulfuric acid</u> is a strong acid, a dehydrating agent, and an oxidizing agent when heated. As a dehydrating agent, it is highly water-reactive, generating tremendous amounts of heat on contact with water. It is very destructive to tissue and metals, and releases flammable hydrogen gas on contact with active metals (e.g., Rb, K, Ca, Mg, Al, Mn, Zn, Fe, Ni, Na). Fuming sulfuric acid is even more hazardous and produces extremely hazardous vapors, and is also a select carcinogen.

<u>Nitric acid</u> is a strong acid and powerful oxidizing agent. It can release hydrogen on contact with most metals. Nitric acid is extremely corrosive and its vapors are toxic. The vapors contain nitrogen oxides that can cause delayed respiratory distress, pulmonary edema (fluid in the lungs), and death. Nitrogen oxides can also be released when nitric acid reacts with metals. Fuming nitric acid is more dangerous than regular nitric acid, again due to the presence of nitrogen oxides. Fuming nitric acid is an acute toxin, as defined in Chapter 22-A.

The <u>halogen acids</u> include hydrofluoric, hydrochloric, hydrobromic, and hydroiodic acid. The corresponding gases, hydrogen fluoride, hydrogen chloride, hydrogen bromide, and hydrogen iodide, are very soluble in water; upon exposure to moisture on the body, formation of the acid occurs. All are strong acids and release hydrogen on contact with active metals.

<u>Hydrofluoric acid</u> is extremely corrosive and attacks glass as well as metal. It is extremely dangerous in all concentrations. It causes severe, slow-healing burns, to tissue that may not be noticed for several hours. It can also cause severe and permanent damage to the respiratory system, including fatal pulmonary edema, and blindness. In addition to these corrosive effects, it can cause delayed systemic poisoning including depletion of tissue calcium and magnesium. It is an acute toxin, as defined in Chapter 22-A, and special handling instructions are included in Appendix H.

<u>Perchloric acid</u> is a strong acid. When heated, it is a strong oxidizing and dehydrating agent; if distilled, dried, or reacted with dehydrating agents or any oxidizable materials, the mixture may spontaneously explode. It forms flammable hydrogen gas on contact with many metals and forms explosive metal perchlorates on contact with certain metals. Perchloric acid is especially hazardous at concentrations above 70%.

<u>Acetic acid</u> is a severe irritant to the skin and eyes. Severe irritation can occur at 25 ppm, but eye damage can occur at lower concentrations. Glacial (100%) acetic acid causes severe eye and tissue damage, is a dehydrating agent, reacts violently with oxidizing agents, and has a flash point of 110°F.

<u>Phenol</u> is a crystalline solid that absorbs moisture from the air. In addition to being corrosive, it is highly toxic and readily absorbed through the skin in liquid and vapor phases. These hazards are compounded by the fact that phenol has an anesthetic effect, so that in some cases, burns have gone unnoticed and untreated for several hours

Sodium and potassium hydroxide are strong corrosives and often referred to as caustics. They are both solids which readily absorb water; and can absorb enough water from the skin to cause severe injury if not washed off immediately. They are both dehydrating agents. They cause severe and permanent eye damage. At low concentrations, the sensation of irritation may not occur for several hours, and can result in severe ulceration. They are even more hazardous in heated solutions.

C. Laboratory Use of Corrosives

- 1. Always investigate the additional hazards such as flammability and reactivity.
- 2. If only a small amount is needed, purchase in small quantities for easier handling and storage.
- 3. Purchase in plastic coated bottles when available.
- 4. Use a bottle carrier or cart or some other means of containment when moving 1 L containers (or larger) of concentrated acids and bases from the stockroom to the laboratory or between laboratories.
- 5. Store separately from incompatible materials.
- 6. Wear appropriate protective equipment, including splash goggles, when using any quantity of concentrated acid or base, and wear lab coats when using more than one liter (see Chapter 4).
- 7. Always add chemicals slowly, and always add acid to water.
- 8. Keep ignition sources away from inorganic acid spills that may produce flammable hydrogen gas on contact with metals, and from glacial acetic acid, which is itself, a fire hazard.

9. When neutralizing corrosives, never add a concentrated acid to base or a concentrated base to acid.

D. Special Precautions for Perchloric Acid

- 1. The following uses of perchloric acid are prohibited without prior approval from the EHS Office:
 - a. Use of perchloric acid at concentrations of 70% or greater;
 - b. Operations involving heating the acid;
 - c. Use of anhydrous perchloric acid.
- Use of concentrated (above 70%) and/or heated perchloric acid, if approved by the EHS Office, is only to be conducted in a special perchloric acid fume hood with a wash down system.
- 3. The number of people using the acid should be limited to the extent possible, and all users should be familiar with the chemistry of the acid, its hazards, proper handling procedures, and emergency procedures.
- 4. Wear splash goggles and nitrile, neoprene, or polyvinyl chloride gloves.
- 5. Perchloric acid should never be used in areas where it would be absorbed by porous surfaces if spilled.
- 6. Perchloric acid should be purchased on an as-needed basis in small containers.
- 7. Perchloric acid must be stored separately from incompatible materials, including organic substances and other combustible materials, in a well-ventilated area.
- 8. All waste should be collected for disposal as hazardous waste.
- 9. Spilled solutions must not be allowed to dry. They should be neutralized and then absorbed with an inert material such as sand or vermiculite. Do not use organic absorbents. The area should then be rinsed with a large quantity of water. The absorbent material should be placed in a container, and the container filled with water and tightly closed. The container should be disposed of as hazardous waste. If a spill is large enough to require the use of respiratory protection, do not attempt to clean it up. Follow evacuation guidelines in Chapter 14.

E. Special Precautions for Hydrofluoric Acid

- 1. Hydrofluoric acid is an acute toxin and, as such, its use requires an SOP. See chapter 6 for more information on Standard Operating Procedures.
- 2. The number of people using the acid should be limited to the extent possible, and all users should be familiar with the chemistry of the acid, its hazards, proper handling procedures, emergency procedures, and all other information in the SOP.
- 3. First aid procedures in Appendix H must be posted in the area of use.
- 4. Calcium gluconate and Honeywell's "Recommended Medical Treatment for Hydrofluoric Acid Exposure" must be available in the area of use. A copy of Honeywell's booklet may be obtained online at http://goo.gl/RKUipe.
- 5. When possible the acid should be purchased at the concentration to be used to avoid preparation of solutions.
- 6. Hydrofluoric acid should be purchased on an as-needed basis in small containers.

- 7. Always use in a functioning fume hood with the sash as low as possible and no higher than 15 inches.
- 8. Only use in a room equipped with an eyewash station and safety shower.
- 9. Keep ignition sources away from the area.
- 10. Wear chemical splash goggles, a face shield providing face and neck protection, neoprene or polyvinyl chloride gloves, and non-absorbent resistant clothing.
- 11. Dispose of protective clothing and wash equipment thoroughly after each use.
- 12. Use only resistant equipment (e.g., polyethylene, Teflon).
- 13. Prior to performing experiments using hydrofluoric acid, disposal procedures should be defined. In general, waste acid should be collected as hazardous waste.
- 14. Small spills should be contained and neutralized with lime prior to disposal.⁵ For large spills, follow evacuation guidelines in Chapter 14 and seek immediate medical attention if necessary.

⁵ Source: National Research Council, 2015. *Prudent Practices in the Laboratory: Handling and Management of Chemical Hazards*. National Academy Press.

Chapter 22: Particularly Hazardous Substances

Chapters 22, 22-A, 22-B, and 22-C deal with the three categories of what OSHA defines as "particularly hazardous substances" (PHSs): acutely toxic substances, select carcinogens, and reproductive toxins. Chapters 22-A, 22-B, and 22-C define and describe specific requirements for working with them. This chapter describes requirements that apply to all three kinds of PHSs.

A. Employee/Student Notification

The supervising faculty member is responsible for informing all employees and students if a substance they are working with is a PHS. Additionally, Standard Operating Procedures (SOPs) must be developed for work with acute toxins, and may also be warranted for work with select carcinogens and/or human reproductive toxins. In such cases, the supervising faculty member is responsible for reviewing the SOP with the employee/student prior to their work with the substance and on an annual basis thereafter.

B. Personal Protective Equipment

<u>Laboratory coats</u>. Laboratory coats should be stocked in all labs that have any PHSs. They must be worn when handling:

- any quantity of an acute toxin
- any quantity of a select carcinogen or reproductive toxin which is readily absorbed through the skin (see the table at the end of chapter 4)
- more than one liter or 500 grams of any other select carcinogen or reproductive toxin

<u>Gloves</u>. If hand contact is possible, gloves appropriate for the task and with resistance to the chemicals handled must be worn. Disposable gloves must be disposed of after every use and must be discarded as hazardous waste immediately after overt contact. Non-disposable gloves must be designated for use only with the PHS they are meant to handle and must be decontaminated after every use.

Eye Protection. Appropriate eye protection must be worn as described in Chapter 4.

C. Personal Hygiene

Hands must be washed with soap and water immediately after overt contact, at the completion of any procedure, and prior to leaving the laboratory. If eyes or other parts of the body are contaminated, wash or flush immediately as described in Chapter 14.

D. Work Area Identification and Access

Each work area or laboratory where PHSs are used on a regular basis must be labeled with one of the Caution signs below:

CAUTION !	CAUTION !
Acute Toxin	Select Carcinogen
In Use in this Area	In Use in this Area
Date:	Date:
Principal Investigator to contact in an emergency:	Principal Investigator to contact in an emergency:
CAUTION ! Potential Reproductive Toxin	
In Use in this Area	
Date:	
Principal Investigator to contact in an emergency:	

When work areas have not been decontaminated or experiments involving PHSs are left in progress, a DO NOT ENTER sign must be posted on the exterior door of the lab, listing the name and phone number of the person to be contacted in case of emergency.

E. Handling and Storage Procedures

Work surfaces

All work surfaces on which non-volatile PHSs are used should be a smooth nonporous material. Porous work surfaces should be covered with stainless steel or plastic trays. The work surface or trays should always be decontaminated after the procedure is complete. When using bench paper, the paper should be replaced and properly disposed of when contaminated.

Containment equipment

Procedures using volatile PHSs and those involving solid or liquid PHSs that may result in the generation of aerosols or airborne particles should be conducted in a fume hood, glove box, or other containment device. Examples of aerosol generation procedures include: transfer operations, blending, open vessel centrifugation, and injection.

Vacuum lines

Vacuum lines, other than water aspirators, should be protected (e.g. with an absorbent or liquid trap and a HEPA filter) to prevent entry of any PHS into the system.

Decontamination

Equipment and contaminated materials should be rinsed with an appropriate solvent. Decontamination of the work area must be done whenever there has been overt contamination and at the end of each experiment. Ideally, the work area should be decontaminated daily. If a work area is not decontaminated prior to leaving for the day, a DO NOT ENTER sign must be posted, as described in Section D above.

F. Waste Disposal

Waste minimization

The experiment should be designed to minimize the amount of waste produced. This may be achieved by using the least amount of the material required and limiting the use of disposable equipment.

Collection for off-site disposal

All waste and contaminated materials must be collected for off-site hazardous waste disposal following the procedures outlined in Chapter 9.

Chapter 22-A: Acute Toxins

A. Defining Acute Toxins

The OSHA Laboratory Standard defines acute toxins, as chemicals which may be fatal as a result of a single exposure or exposure of short duration. The OSHA Hazard Communication Standard⁶ defines a similar category, "highly toxic chemicals," based on animal toxicity data using the following criteria.

> Oral LD₅₀ (rats) \leq 50 mg/kg Skin Contact LD₅₀ (rabbits) \leq 200 mg/kg Inhalation LC₅₀ (rats) \leq 200ppm/1hr

The Globally Harmonized System (GHS) of Classifying and Labeling Chemicals defines four categories of acute toxins, in order of decreasing severity:

Acute Toxicity							
type	Category 1	Category 2		Category 3		Category 4	
Acute Toxicity, Oral (mg/kg)	≤ 5	> 5	≤ 50	> 50	≤ 300	> 300	≤ 2000
Acute Toxicity,	< 50	> 50	< 200	> 200	≤ 1000	> 1000	≤ 2000
Dermal (mg/kg)							
Acute Toxicity,							
Inhalation - Gases	≤ 100	> 100	≤ 500	> 500	≤ 2500	> 2500	≤ 5000
(ppm)							
Acute Toxicity,							
Inhalation - Vapors	≤ 0.5	> 0.5	≤ 2.0	> 2.0	≤ 10	> 10	≤ 20
(from liquid) (mg/l)							
Acute Toxicity,							
Inhalation - Dust &	≤ 0.05	> 0.05	≤ 0.5	> 0.5	≤ 1.0	> 1.0	≤ 5
Mist (solids) (mg/l)							

Table 22a.1: GHS classification of acute toxins, based on LD₅₀ or LC₅₀

For the purposes of this Chemical Hygiene Plan, substances that meet the criteria for GHS Acute Toxicity (oral, dermal, or inhalation) Category 1 or 2 shall be considered acute toxins, as they also meet the definition of "highly toxic chemicals" under the OSHA Hazard Communication Standard. The GHS acute toxicity category can be found on a Safety Data Sheet. A substance shall also be considered an acute toxin if the faculty member has knowledge that it should be treated as such.

⁶OSHA Hazard Communication Standard, 29 CFR 1910.1200.

Category 1 and 2 acute toxins carry one or more of the following hazard codes (H codes):

- H300 Fatal if swallowed
- H310 Fatal in contact with skin
- H330 Fatal if inhaled

GHS Acute Toxicity Category 1, 2, and 3 substances will bear the following GHS pictogram.



Materials in which sodium azide is used in small amounts as a preservative shall not be regarded as acute toxins.

B. Standard Operating Procedures

A written Standard Operating Procedure (SOP) is required for any use of a Category 1 or Category 2 acute toxin. Some template protocols have been developed and are available that may only require customization for the specific use of the substance. The SOP is to be kept in the lab's Safety Binder. If a student is to be working with an acute toxin, the faculty member must familiarize the student with the SOP for the use of that substance and specific experimental procedure. This training will be documented in the lab's Safety Binder.

Chapter 22-B: Select Carcinogens

A. Defining Select Carcinogens

These guidelines for the laboratory use of carcinogens establish procedures and safeguards for minimizing exposure of laboratory personnel to substances that pose a carcinogenic risk. They apply to all substances defined as "select carcinogens" by the OSHA Laboratory Standard and include:

- all OSHA regulated carcinogens (29 CFR Subpart Z),
- all substances listed by the National Toxicology Program (NTP) as "known to be carcinogens",
- all substances defined by the International Agency for Research on Cancer (IARC) as Group 1, "carcinogenic to humans",
- all substances listed by the NTP as "reasonably anticipated to be carcinogens", and
- all substances listed by the IARC as Group 2A, "probably carcinogenic to humans" or 2B, "possibly carcinogenic to humans".

Appendix Q (Summary of Particularly Hazardous Substances) lists select carcinogens from the sources listed above.

In the GHS system, select carcinogens are designated by one of the following hazard statements:

H350 May cause cancer H351 Suspected of causing cancer

These statements are found on the SDS and manufacturer labels. Substances with SDSs that contain either of these statements will be handled as Select Carcinogens, as outlined in Chapter 22. The SDS and manufacturer container will also bear the following GHS pictogram, which warns of several hazards in addition to carcinogenicity.



B. Special Requirements for Formaldehyde

OSHA has established a separate Standard for formaldehyde, 29 CFR 1910.1048 that applies to laboratories as well as other users of formaldehyde. Under that Standard employee exposure monitoring is required to determine if a particular experiment results in overexposure to formaldehyde. As with the requirements of the OSHA Laboratory Standard, the same standards of protection with regard to formaldehyde exposure will be applied to students.

To accomplish the required monitoring, faculty members should notify the EHS Office at least 2 weeks before any experiment where formaldehyde is used in concentrations greater than 0.1%. The EHS Office shall assess the potential for respiratory exposure. In general, potential should be minimized by pre-rinsing specimens, using formalin-free products whenever possible, and providing effective ventilation by using fume hoods or down-draft tables.

If monitoring has been conducted in previous semesters for that experiment, notification is not required unless the EHS Office has informed the faculty member that additional monitoring is necessary. Additional requirements of the Standard may apply based on the results of monitoring, and these requirements will be discussed with individual faculty members as needed.

The Formaldehyde Standard also establishes hazard communication requirements, labeling, SDS, and training for the use of all solutions greater than 0.1% or materials capable of releasing formaldehyde in excess of 0.1 ppm.

<u>Labeling</u>

For products containing 0.1% to 1%, or capable of releasing 0.1 to 0.5 ppm, labels must include a warning that the product contains formaldehyde and that more information is available on the SDS. The label below is to be used and is available at the Department offices.

Contains FORMALDEHYDE (less than 1 percent) Consult SDS for hazard information.

For products containing more than 1%, or capable of releasing greater than 0.5 ppm, the label must also address health hazards and include the words "Potential Cancer Hazard". The label below is to be used and is available at the Department offices.

Contains FORMALDEHYDE Estimated Percent:_____ POISON POTENTIAL CANCER HAZARD Harmful if swallowed, inhaled or absorbed through the skin. May cause allergic skin or respiratory system reactions. Contact with skin or eyes may cause severe irritation or burns. Ingestion may cause severe burning to the mouth and stomach.

> AVOID BREATHING VAPORS AVOID SKIN OR EYE CONTACT Consult SDS for additional information

Products purchased after December 1992 should be properly labeled by the vendor. Products purchased before that date or are in secondary containers must be labeled with the appropriate warning.

<u>SDS</u>

Safety Data Sheets must be readily accessible for all formaldehyde containing products as described in Chapter 2.

<u>Training</u>

Annual training is required for all formaldehyde product users. That training is the responsibility of the supervising faculty member. Specific requirements are described in Chapter 13.

Chapter 22-C: Reproductive Toxins

Reproductive toxins, one of OSHA's three categories of Particularly Hazardous Substances, are substances that affect reproductive capability and include four general categories.

- 1. <u>Mutagens</u>: Substances that may cause a change (mutation) in the genetic material of a cell.
- 2. <u>Teratogens</u>: Substances that may affect the viability or cause physical or metabolic defects in the developing embryo or fetus when a pregnant female is exposed to that substance.
- 3. <u>Sterility/Infertility</u>: Substances that may affect female or male fertility.
- 4. <u>Lactation</u>: Substances that may be transferred from the mother to the child through the breast milk and cause adverse health effects in the child.

Reproductive toxins include physical agents (e.g. radiation), biological agents (e.g. viruses), maternal metabolic imbalances, and chemical agents.

In the GHS system, reproductive toxins are designated by one or more of the following hazard statements:

- H340 May cause genetic defects
- H341 Suspected of causing genetic defects
- H360 May damage fertility or the unborn child
- H361 Suspected of damaging fertility or the unborn child
- H362 May cause harm to breast-fed children

These statements are found on the SDS and manufacturer labels. Substances with SDSs that contain any of these statements will be handled as Reproductive Toxins, as outlined in Chapter 22. The SDS and manufacturer container will also bear the following GHS pictogram, which warns of several hazards in addition to reproductive toxicity.



A large number of substances have been reported to be animal reproductive toxins in various species. There is no established method for defining when animal evidence is sufficient to relate to human reproductive toxicity potential. Precautions should be taken to minimize exposure to all reproductive toxins particularly during pregnancy.

The list at the end of this chapter contains examples of chemicals known or suspected to be human reproductive toxins. The list does not take into account the chemical form, concentration, toxicity, or length of exposure.

As there is no definitive list of human reproductive toxins, they will be defined here as a substance which meets one of the following criteria.

- 1. It appears in Table 22c.1.
- 2. The container label or Safety Data Sheet reports positive findings of human reproductive toxicity.
- 3. The faculty member using it has knowledge that the substance is a human reproductive toxin.

Table 22c.1: Examples of known or s	uspected human reproductive toxins
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MUTAGENS	dimethylformamide "s"	naphthylamine, 2- "s"
acrolein "s"	dimethylhydrazine, 1,1-"s"	naphthylmethylcarbamate
acrylonitrile "s"	dimethylhydrazine, 1,2- "s"	methimazole
aminoazotoluene, o-	dinitropyrene, 1,6-	nickel sulfide
aminodiphenyl, 4- "s"	dinitropyrene, 1,8-	nitrofluorene
auramine	endosulfan "s"	nitrogen mustard and cmpds "s"
azathioprine	epichlorohydrin "s"	nitropyrene, 1-
benzene "s"	ethidium bromide	nitroso-n-methylurea, n-
benzo(a)pyrene	ethyl-n-nitrosourea, N-	nitrosodi-n-butylamine, n-
bischloroethylnitrosourea	ethyl methanesulphonate	nitrosodi-n-propylamine, n-
bromodichloromethane	ethylene dibromide "s"	nitrosodiethylamine, n-
chloramphenicol	ethyleneimine "s"	nitrosodimethyamine, n-
chlordane and isomers "s"	formaldehyde "s"	nitrosomorpholine, n-
chloro-2-methylpropene, 3-	furylamide	nitrosopiperidine, n-
chloro-o-phenylenediamine, 4-	GLU-P-1 and 2	nitrosopyrrolidine, n-
chloro-o-toluidine, 4-	glycidol "s"	norethisterone
chloroform	gossypol	ozone
chloromethyl ether, bis "s"	grisofulvin	parathion "s"
chloromethyl methyl ether	heptachlor "s"	phenobarbital
chloroprene "s"	heptachlor epoxide "s"	potassium chromate (VI)
cisplatin	hexamethylphosphoramide "s"	potassium dichromate (VI)
colchicine	hydrazine "s"	propane sultone, 1,3- "s"
daunomycin	hydrazine sulfate "s"	propiolactone, beta
diaminoanisole, 2,4-	lasiocarpine	propylene oxide
diaminotoluene, 2,4-	lead and compounds	propylthiouracil
dibenz(a,h)anthracene	medroxyprogesterone acetate	safrole
dibromo-3-chloropropane, 1,2- "s"	methylaminopterin	sodium azide "s"
dibromopropyl (2,3) phosphate "s"	methyl bromide "s"	sodium dichromate IV "s"
dichlorobenzidine, 3,3- "s"	methyl hydrazine "s"	sterigmatocystin
dichloroethane, 1,2- "s"	methyl methane sulfonate	streptozotocin
dichloromethane	methylazeridine, 2- "s"	styrene "s"
dichlorvos "s"	methylazoxymethyl acetate	styrene, 7,8-oxide "s"
diepoxybutane "s"	metronidizol	thio-tep
dimethyl aminoazobenzene, 4-	mitomycin C	thioacetimide
dimethyl sulfate "s"	MNNG	thiourea
dimethyl sulfoxide "s"	monocrotaline	toluene "s"
dimethylcarbamoyl chloride	mustard gas "s"	toluene diisocyanate, 1,3-

22-C: Reproductive Toxins

toxaphene "s" treosulfan trichlorethylene TRP-P-2 urethane vinyl acetate vinyl chloride zinc chromate hydroxide zinc chromate hydroxide hydrate

TERATOGENS

2,4,5-T "s" aminonicotinamide, 6aminopteridine arsenic and compounds "s" bisulfan cadmium and compounds carbon disulfide "s" carbon monoxide chlorambucil chloroprene "s" cyclophosphoramide DDT "s" diazepam "s" diethylstilboestrol "s" dimethanesulfonate, 1,4ethylene dibromide "s" ethylene glycol ethers ethylene oxide fowler's solution

halothane lead and compounds lithium and compounds medroxyprogesterone acetate mercury and compounds "s" methimazole methylaminopterin methylthiouracil nicotine "s" paramethadione penicillamine phenobarbital phenytoin polybrominated biphenyls "s" polychlorinated biphenyls "s" progesterone propylthiouracil reserpine retinoic acid, 1,3-cistamoxifin TCDD "s" tetracyclines thalidomide "s" tobacco smoke(not passive) toluene "s' trimethadione valproic acid warafin "s"

bisulfan cadmium and compounds carbon disulfide "s" chloroprene "s" DDT "s" dibromo-3-chloropropane "s" diethylstilboestrol, "s" ethylene dibromide "s" ethylene glycol ethers gossypol kepone "s" lead and compounds melphalen mercury and compounds "s" mestranol mirex "s" naphthyl methylcarbamate norethisterone phenoxybenzamine hydrochloride polychlorinated biphenyls "s" tobacco smoke (not passive) vinyl chloride

LACTATION

hexachlorobenzene "s" lead and compounds methyl mercury and cmpds "s" polychlorinated biphenyls "s" tetrachloroethylene "s"

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FERTILITY

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Chapter 23: Nanomaterials

Nanoparticles and nanomaterials have different reactivities and interactions with biological systems than bulk materials, and understanding and exploiting these differences is an active area of research. However, these differences also mean that the risks and hazards associated with exposure to engineered nanomaterials are not well known. Because this is an area of ongoing research, consult trusted sources for the most up to date information available. Note that the higher reactivity of many nanoscale materials suggests that they should be treated as potential sources of ignition, accelerants, and fuel that could result in fire or explosion. Easily dispersed dry nanomaterials may pose the greatest health hazard because of the risk of inhalation. Operations involving these nanomaterials deserve more attention and more stringent controls than those where the nanomaterials are embedded in solid or suspended in liquid matrixes.

Consideration should be given to all possible routes of exposure to nanomaterials including inhalation, ingestion, injection, and dermal contact (including eye and mucous membranes). Avoid handling nanomaterials in the open air in a free-particle state. Whenever possible, handle and store dispersible nanomaterials, whether suspended in liquids or in a dry particle form, in closed (tightly-sealed) containers. Unless cutting or grinding occurs, nanomaterials that are not in a free form (encapsulated in a solid or a nanocomposite) typically will not require engineering controls. If a synthesis is being performed to create nanomaterials, it is not enough to only consider the final material in the risk assessment, but consider the hazardous properties of the precursor materials as well.

It is preferable to keep particles fixed in a matrix or bound in a solution. Storage and use of free particles should be done as a last resort. Follow the standard hierarchy of hazard controls for nanoparticles: substitution, isolation, and ventilation. To minimize laboratory personnel exposure, conduct any work that could generate engineered nanoparticles in an enclosure that operates at a negative pressure differential compared to the laboratory personnel breathing zone. Limited data exist regarding the efficacy of PPE and ventilation systems against exposure to nanoparticles. However, until further information is available, it is prudent to follow standard chemical hygiene practices. The faculty member in charge of the lab will conduct a hazard evaluation to determine PPE appropriate for the level of hazard according to the requirements set forth in OSHA's Personal Protective Equipment standard (29 CFR 1910.132).

Appendices

Appendix A: Chemical Standard Operating Procedure

Appendix B: Laboratory Standard Operating Procedure

Appendix C: American Chemical Society's Risk Assessment Matrices, F-2 & F-3

Appendix D: Example SOPs

Appendix E: Permission to Work After Hours Form
Appendix F: Visiting Researcher Form

Appendix G: Student Injury Report Form

Appendix H: First Aid Treatment for Hydrofluoric Acid Exposure

Appendix I: Chemical Compatibility Chart

Appendix J: Laboratory Inspection Checklist

Appendix K: Student NMR Safety Agreement

Appendix L: U- and P-Listed Wastes

Appendix M: F-Listed Solvent Waste

Appendix N: D-Listed Characteristic Waste

Appendix O: Rhode Island DEM Hazardous Waste Regulations (excerpt)

Appendix P: Rhode Island DEM Medical Waste Regulations (excerpt)

Appendix Q: Summary of Particularly Hazardous Substances

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