

Massachusetts Institute of Technology
Department of Chemistry

Chemical Hygiene Plan and Safety Manual 2019



CAUTION
WEAR FACE SHIELD,
HYDROGEN GLOVES AND
PFRON WHILE USING
FILL STATION



Chemistry

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
DEPARTMENT OF CHEMISTRY

*Chemical Hygiene Plan
and
Safety Manual*

2019

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2019

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Chemical Hygiene Plan
Twenty-Ninth Edition, 2019
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Section One: Chemical Hygiene Plan

Part I. Introduction

A. Policy

It is the policy of the Massachusetts Institute of Technology (as represented by the MIT Corporation and the Office of the President) to provide a safe and healthy workplace in compliance with the Occupational Safety and Health Act of 1970 and regulations of the Department of Labor including 29 CFR 1910.1450 “Occupational Exposure to Hazardous Chemicals in Laboratories” (the “Laboratory Standard”). The full Laboratory Standard is included as Appendix A of this Chemical Hygiene Plan.

B. Purpose

This document constitutes the Chemical Hygiene Plan required by the above regulation. The purpose of the Plan is to describe proper practices, procedures, equipment, and facilities to be followed by employees, students, visitors, and other personnel working in each laboratory of the Department in order to protect them from potential health hazards presented by chemicals used in the workplace, and to keep exposures below specified limits. It is the responsibility of the faculty, administration, and research and supervisory personnel to know and to follow the provisions of this Plan.

This Plan also includes a discussion of emergency action procedures as required under OSHA Standard 29 CFR 1910.38 (“Employee Emergency Plans and Fire Prevention Plans”).

C. Personnel Covered by this Plan

This Chemical Hygiene Plan applies to all work involving hazardous substances that is conducted in space assigned to the Department of Chemistry as defined in the MIT Institute Report Room List. Visitors and individuals holding appointments in other MIT departments who plan to conduct research involving hazardous substances in Chemistry Department laboratories must undergo the chemical hygiene training outlined in Part III and file a Chemical Hygiene Clearance Form to Scott Ide (18-281) before beginning work.

Acknowledgment

Portions of this Chemical Hygiene Plan were drawn from the manual: “*Prudent Practices for Handling Hazardous Chemicals in Laboratories*,” prepared by the National Academy of Sciences’ Committee on Hazardous Substances in the Laboratory (National Academy Press, Washington, D.C., 1981) and “*Prudent Practices in the Laboratory*” (National Academy Press, Washington, D.C., 1995).

Part II. Responsibility, Authority, and Resources

A. Department Head

The Department Head has the responsibility and the authority to see that the Chemical Hygiene Plan is written, updated, and implemented. In addition, the Department Head appoints the EHS Committee and Chemical Hygiene Officer in accordance with the definition provided in paragraph (b) of 29 CFR 1910.1450 and the requirements outlined in section II-B of this document. The Department Head has the final responsibility for the safety and health of the employees, visitors, students, and other personnel conducting work in the Chemistry Department.

B. EHS Committee, EHS Coordinator, and Chemical Hygiene Officer

The EHS Committee assists the chairperson with the development and implementation of the Department's Chemical Hygiene Plan (CHP). The EHS Committee provides advice and assistance to laboratory supervisors with regard to the training of Chemistry Department personnel and the implementation of the CHP.

Members of the Chemistry Department EHS Committee (2019)

Professor Rick L. Danheiser, Chair	18-298	x3-1842
Professor Stephen Buchwald	18-490	x3-1885
Kenny Chen (<i>Student Member</i>)	56-546	x4-1871
Professor Gabriela Schlau-Cohen	6-225	x3-1478
Professor Christopher Cummins	6-435	x3-5332
Kyan D'Angelo (<i>Student Member</i>)	18-132	x4-0394
Joseph Dennis (<i>Student Member</i>)	18-343	x4-0261
Dr. John Dolhun (<i>Director, Undergraduate Laboratories</i>)	12-5220	x8-6848
Luis Galindo (<i>Laser Biomedical Research Center</i>)	6-204	x3-6203
Scott Ide (<i>EHS Coordinator and Chemical Hygiene Officer</i>)	18-281	x4-6132
Jun Jiang (<i>Student Member</i>)	6-426	x4-2056
Corey Kaminsky (<i>Student Member</i>)	18-163	x8-7268
Jared Matos (<i>Student Member</i>)	6-426	x4-2056
Professor Mohammad Movassaghi	18-290	x3-3986
Professor Ronald T. Raines	18-498	x3-1470
Carly Schissel (<i>Student Member</i>)	18-572	x4-1841
Professor Matthew Shoulders	16-573a	x2-3525
Dr. Richard Wilk (<i>Administrative Officer</i>)	18-390	x3-1802

The responsibilities of the Chemistry Department EHS Coordinator include providing initial EHS training to new personnel and assisting in refresher training, administering the laboratory inspection program, serving as the Chemistry Department Emergency Action Coordinator and Fire Marshal, providing advice and assistance to Chemistry Department personnel on various EHS matters, and overseeing training, accident, and inspection recordkeeping for the department. Additionally, the EHS Coordinator acts as the Chemical Hygiene Officer.

C. Laboratory Supervisors

The Supervisor's duties, as defined in the OSHA Laboratory Standard and the MIT Chemical Hygiene Plan, are the responsibility of the faculty member (principal investigator) in charge of each laboratory. In addition, the following Department personnel also have supervisory responsibilities as indicated:

Instrumentation Facility	Dr. Walter Masefski
X-Ray Laboratory	Dr. Peter Mueller
Undergraduate Laboratories	Dr. John Dolhun

The primary responsibility of the supervisor is to implement the Chemical Hygiene Plan and ensure compliance with the OSHA Laboratory Standard. The supervisor's duties include (but are not limited to) the following:

1. Instruct all personnel to conduct work in accordance with the Department's Chemical Hygiene Plan;
2. Define the location of designated areas for work with particularly hazardous substances (see Part VI) and ensure that an inventory of these substances is properly maintained;
3. Review and approve standard operating procedures for work involving hazardous substances;
4. Define hazardous operations, designating safe practices and specifying protective equipment;
5. Ensure that all staff receive instructions and training in safe work practices, use of safety equipment, and procedures for dealing with accidents involving hazardous substances;
6. Direct all personnel to obtain the medical examinations and protective equipment necessary for the safe performance of their job;
7. Monitor the safety performance of personnel with regard to required safety practices and techniques. Supervisors can deny access to laboratories to personnel who fail to comply with safety policies.
8. When required, arrange for workplace air samples, swipes, or other tests to determine the amount and nature of airborne and/or surface contamination, inform employees of the results, and use data to aid in the evaluation and maintenance of appropriate laboratory conditions;
9. Assist and cooperate with members of the MIT Environmental Health and Safety Office when necessary;
10. Ensure that Level I inspections are conducted weekly to monitor compliance with existing laboratory procedures and regulations;
11. Formulate procedures for dealing with accidents that may result in the unexpected exposure of personnel or the environment to toxic substances;
12. Investigate accidents and report them to the Chemical Hygiene Officer. Institute procedures that will minimize the repetition of accidents;
13. Report to the Chemical Hygiene Officer incidents that cause (1) personnel to be seriously exposed to hazardous chemicals or materials, or that (2) constitute a danger of environmental contamination;
14. Take action to correct work practices and conditions that may result in the release of toxic chemicals;

15. Instruct laboratory personnel to properly dispose of unwanted and/or hazardous chemicals and materials;
16. Make copies of the approved safety plan and Chemical Hygiene Plan available to the program and support staff;
17. Provide refresher training and conduct periodic examinations to monitor the familiarity of research personnel with the provisions of the CHP and with group safety rules and standard operating procedures. Appendix 2 of this plan includes a list of chemical hygiene questions that should be relevant to most work involving hazardous substances in the department;
18. Arrange for non-laboratory personnel (e.g. contractors and support personnel) to be informed of potential hazards they may be exposed to when working in your laboratory, and provide proper instruction to minimize the risk of harmful exposure to hazardous substances.

D. Group EHS Representatives and Fire Wardens

It is the responsibility of every faculty member to appoint a Group EHS Representative and Fire Warden for their research laboratory. Group EHS Representatives advise and assist their laboratory supervisors in training new personnel, disseminating safety information, conducting Level I inspections of their group's laboratories, and inspecting and ensuring the maintenance of group safety equipment such as spill control kits, fire extinguishers, safety showers, and eyewash facilities. The Group EHS Representative's responsibilities include, but are not limited to, safety issues involving chemical hygiene. Group EHS Representatives are also responsible for evaluating and making recommendations on safety issues that concern the entire department. The responsibilities of Fire Wardens include familiarizing members of their laboratory with emergency and evacuation procedures, carrying out monthly visual inspections of the emergency equipment in their laboratory, and conducting "sweeps" of their work area during evacuations to verify that everyone has left the building.

E. Employees, Staff, and Research Personnel

Employees, as defined by the MIT Chemical Hygiene Plan, are those staff under the direction of the Supervisor, as defined by the plan. Employees not under the direction of the Supervisor, but who are in an area under the direction of the Supervisor, are also subject to the MIT Chemical Hygiene Plan and the standard operating procedures in effect in that area. Also subject to the plan are all "non-employee" personnel including graduate and undergraduate students, postdoctoral fellows, visiting scientists, research affiliates and temporary workers.

It is the responsibility of employees and other research personnel to follow the procedures outlined in the MIT Chemical Hygiene Plan and all standard operating procedures developed under that plan. Failure to comply with safety procedures could result in researchers being denied access to department laboratories where hazardous chemicals are in use until they have demonstrated the ability to work safely. The responsibilities of research personnel include the following:

1. Understand and follow all standard operating procedures;
2. Understand all training received;
3. Understand the function and proper use of all personal protective equipment and wear personal protective equipment when mandated or necessary;

4. Report, in writing to your supervisor, any significant problems arising from the implementation of the standard operating procedures;
5. Report to your supervisor and the Department Chemical Hygiene Officer all facts pertaining to every accident that results in exposure to toxic chemicals, and any action or condition that may exist that could result in an accident. Prepare written reports describing the circumstances of all serious accidents as discussed in detail in Part X-D of this plan;
6. Contact your supervisor, the Chemical Hygiene Officer, or the EHS Office if any of the above procedures are not clearly understood.

It is the responsibility of researchers to make a determination as to whether they have sufficient knowledge and experience to carry out an experiment safely. This is a necessary step in the risk assessment performed prior to carrying out every experiment. If a researcher has any doubt as to whether they understand the proper procedures to carry out an experiment safely, they should not proceed and should seek advice from their laboratory supervisor, their EHS Coordinator (Scott Ide), and/or the EHS Office.

F. Environmental Health and Safety Office

The **Environmental Health and Safety Office (EHS)** is the component of the Environmental Programs Office (EPO) charged with responsibility for control, review, monitoring, and advice with respect to work with chemical, radiological, and biological agents used in research and teaching. The EHS Office is comprised of five programs, including Industrial Hygiene, Biosafety, Radiation Protection, Environmental Management, and Safety. **Environmental Management** is charged with responsibility for chemical waste disposal and all matters connected to compliance with environmental protection regulations. All of these offices have authority to stop any activity that in their judgment is immediately hazardous to life or health. In addition, **Radiation Protection** has regulatory authority as part of MIT's license to use radioactive materials from the Massachusetts DPH Radiation Control Program. In addition, the EHS Office has professional staff that can be called upon for advice and help on safety and environmental health problems. Safety evaluates and implements safety policies and reviews new and existing equipment and operating practices to minimize hazards to the Institute community and visitors from fire, electricity, explosion, pressure, and machinery. The EHS Office conducts accident investigations, and suggests remedial measures and procedures. Environmental Management is responsible for ensuring that MIT complies with environmental regulations and also manages the waste chemical service that picks up hazardous and waste chemicals. The EHS Office website is <http://ehs.mit.edu>.

The services of all five programs of the EHS Office are available both in emergency situations and in an advisory capacity to answer questions from anyone at the Institute. All services provide 24-hour on-call personnel to respond to off-hours needs. They can be reached off hours through Operations Center (253-1500) and during daytime hours by calling 2-EHSS. **Dial 100** for Assistance in any **Emergency**.

Part III. Information and Training

A. Initial Training and Refresher Training

All members of the Chemistry Department should be familiar with the hazards associated with the chemicals present in their work area. Researchers whose work involves the use of hazardous substances must be informed as to the proper handling procedures and measures they must take to protect themselves from these hazards. Consequently, MIT and the Department of Chemistry have developed a series of training requirements. All new personnel in the Department of Chemistry must complete the Training Needs Assessment which is accessible through the EHS Office's website at <http://ehs.mit.edu/site/training>. An MIT Certificate is required along with a Kerberos username and MIT I.D. Verify that the user information is correct and complete the Training Needs Assessment. This will generate a list of training requirements. Virtually all researchers (with the exception of some theoretical chemists) will be required at a minimum, to complete the following steps prior to beginning work in areas where hazardous chemicals are in use. **Even if you do not work in areas where hazardous chemicals are in use, you still need to complete step 5, listed below.**

1. New personnel must attend the Chemical Hygiene and Safety Lecture presented in January or take the on-line version, Chemical Hygiene & Safety for Chemists, EHS00101w.
2. Read and understand the Chemistry Department's Chemical Hygiene Plan and Safety Manual.
3. Receive Initial Lab Specific Chemical Hygiene and Safety Training from your Laboratory Supervisor or their designee (you will need to obtain the Laboratory Supervisor's signature on the EHS Clearance form). See below for more information.
4. Complete the training course, Managing Hazardous Waste. This is offered as a web based course and is accessible through the training website mentioned above. This is an annual requirement. As the expiration date approaches, an automatic e-mail reminder will be sent to indicate that you must log on to the training website and complete the web course again.
5. New members of the Department must sign the EHS Clearance Form and submit it to Scott Ide (18-281), indicating that all training requirements stated on the form have been met. The laboratory supervisor must also sign the form.

New graduate students are required to submit their EHS Clearance Form by the end of January of their first year or when they first begin laboratory work (whichever comes first). **Other research personnel** (including postdocs, visiting scientists, technicians, and undergraduate students) must submit their EHS Clearance Form within two weeks of the beginning of their appointment. Completed forms will be kept on file in the office of the EHS Coordinator. In the event that a completed form is not submitted on time as required above, then the worker and their supervisor will be notified in writing by the Department Administrative Officer that the individual is not authorized to work in areas where hazardous substances are in use.

The hazards present in the laboratories of the Chemistry Department vary widely from group to group, and consequently it is the **responsibility of the laboratory supervisor** to provide personnel working in their groups with proper information and training on hazardous chemicals. In addition to this specific training, some personnel are also required to participate in certain safety seminars and training programs. For example, **laboratory course teaching assistants** are required to attend a special Chemistry Department safety training session in September, and undergraduate students enrolled in chemistry laboratory courses must attend the special training sessions conducted in each course at the beginning of each semester.

Each research group must hold a refresher meeting to review chemical hygiene and safety procedures, and emergency action procedures at least once each year. A list of personnel attending these refresher training sessions should be compiled and forwarded to the EHS Coordinator (Scott Ide, Room 18-281). Groups should also conduct periodic written or oral examinations to monitor the familiarity of research personnel with the provisions of the CHP and with group safety rules and standard operating procedures. Appendix 2 of this plan includes a list of chemical hygiene questions that should be relevant to most work involving hazardous substances in the department.

B. Information on Hazardous Substances

It is the responsibility of all researchers to be familiar with the health and physical hazards of all chemicals involved in their work. Information on hazardous chemicals and procedures for handling them can be obtained from books available in the Science Library, the Chemistry Department Library of Lab Safety (see below), and the MIT EHS Office (N52-496). Safety Data Sheets (see below) are another valuable source of information. Additional information on hazardous chemicals can be obtained by contacting the MIT Industrial Hygiene Program (N52-496, 452-3477).

The Chemistry Department's **Library of Lab Safety** (Building 18, 2nd floor next to copy machine) is maintained by the EHS Coordinator. Information on hazardous chemicals is available in the following references in the Library of Lab Safety:

Prudent Practices in the Laboratory: Handling and Disposing of Chemicals, prepared by the National Research Council, 1995 publication. (The 1995 publication has a blue cover and is 427 pages. Every group should have their own copy; additional copies are available in Chemistry Headquarters. This is the version of the safety manual that is referred to in the OSHA Lab Standard as the model for Chemical Hygiene Plans.)

Prudent Practices in the Laboratory: Handling and Management of Chemical Hazards prepared by the National Research Council, 2011 publication. (The 2011 publication has a red cover, is 337 pages of text and includes a supplemental CD. This second edition has a focus on developing a safety culture, provides an updated guide to federal regulations, and covers new areas that include nanotechnology, emergency planning and laboratory security.)

Handbook of Laboratory Safety (Third edition), A. K. Furr, Ed., 1989. (A 704 page reference on all aspects of lab safety).

A Comprehensive Guide to the Hazardous Properties of Chemical Substances, P. Patnaik, 1992. (763 pages describing general properties, health, fire, and explosion hazards, exposure limits, and disposal procedures for more than 1,500 specific compounds. Organized in chapters by compound class, and each chapter includes a general overview of the hazards of that family of chemicals. Probably the single most useful reference on laboratory handling of hazardous substances).

Chemical Safety Data Sheets, Royal Society of Chemistry, 5 volumes, Cambridge, UK, 1989–1992. An excellent collection of summaries of hazard information on more than 500 chemicals.

The Sigma-Aldrich Library of Chemical Safety Data (Second Edition), R. E. Lenga, Ed., 2 volumes, 1988. (This 4,098 page work provides information on the properties of over 14,000 compounds. Toxicity data, health hazards, and suggested methods of first aid, handling, storage, and waste disposal are also included).

Chemical Hazards of the Workplace (Third Edition), G. J. Hathaway, N. H. Proctor, J. P. Hughes, and M. L. Fischman, 1992. (665 pages; includes fairly detailed discussions of the toxicology of 542 hazardous substances).

Toxic and Hazardous Industrial Chemicals Safety Manual prepared by the Japanese International Technical Information Institute, 1988. (700 pages; safety data on 702 compounds).

Safety in the Chemical Laboratory Edited by N. V. Steere and M. M. Renfrew, 4 volumes, 1967–1981 (collection of articles from “Safety in the Chemical Laboratory” feature of the Journal of Chemical Education).

Prudent Practices for Disposal of Chemicals from Laboratories, prepared by the National Research Council, 1983. (282 pages; every group should have their own copy).

Rapid Guide to Hazardous Chemicals in the Workplace, Second Edition, R. J. Lewis, Ed., 1990. (Concise compilation of properties and safety data (PELs, TLVs, etc.) for 800 substances).

Destruction of Hazardous Chemicals in the Laboratory, G. Lunn and E. B. Sansone, 1990. (Detailed procedures for destruction of hazardous substances via chemical reactions).

Handbook of Reactive Chemical Hazards Third Edition, L. Bretherick, 1985. (The best compilation of information on the hazards of reactive and explosive materials. Information on the stability, explosibility, and incompatibilities of over 9,000 compounds is included).

Safety Data Sheets (SDS’s) are valuable sources of information on hazardous substances. An SDS typically includes information on a compound’s physical properties (boiling point, odor, appearance) and also contains data concerning health hazards (exposure limits, symptoms of exposure, first aid), fire and explosion hazards (flash point, recommendations on extinguishing fires), chemical reactivity, and recommended methods for handling storage, spill control, and waste disposal.

Federal law requires that suppliers send an SDS to MIT the first time a compound is ordered by a student or employee. Safety Data Sheets are also available on the World Wide Web; a link to an excellent collection of SDSs is included on the MIT Safety Program website at <http://ehs.mit.edu/site/chemical-safety/sds-and-chemical-safety-information>.

Laboratory Chemical Safety Summaries (LCSSs) provide information similar to that found in an SDS, but these documents are specifically designed for use by laboratory workers. Included in an LCSS are the key physical, chemical, and toxicological data necessary to evaluate the relative degree of hazard posed by a substance. LCSSs also include a concise critical discussion, presented in a style readily understandable to laboratory workers, of the toxicity, flammability, reactivity, and explosibility of the chemical; recommendations for the handling, storage, and disposal of the title substance; and first aid and emergency response procedures. The 1995 edition of Prudent Practices contains LCSSs for 88 chemical substances. PubChem website has a listing of more LCSSs, which may be accessed at the following link: <https://pubchem.ncbi.nlm.nih.gov/lcss/>

NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards (Mackison, F. W.; Stricoff, R. S.; Partridge, L. J., Eds.; DHHS (NIOSH) Publication No. 81-123; U.S. Govt. Printing Office: Washington, D.C., 1981 and supplements published as DHHS (NIOSH) Publication No. 89-104; U.S. Govt. Printing Office: Washington, D.C., 1988) are also very useful sources of information on hazardous substances. NIOSH Guidelines are currently available for almost 400 substances and are based on the information assembled under the Standards Completion Program which served as the basis for the promulgation of Federal occupational health regulations (“substance-specific standards”). Each guideline is typically 5 pages in length and is written clearly in plain language at a level which should be readily understood by laboratory workers. Guidelines include information on physical, chemical, and toxicological properties, signs and symptoms of exposure, and considerable detail on control measures, medical surveillance practices, and emergency first aid procedures. However, note that some guidelines date back to 1978 and may not be current, particularly with regard to chronic toxic effects. Copies of NIOSH Guidelines can be obtained from the Industrial Hygiene Program.

Part IV. Protective Equipment

This section of the Chemical Hygiene Plan discusses equipment and personal apparel that may be required to protect researchers from the hazards presented by certain chemicals. Note that the standard operating procedures for work with specific hazardous substances often also include special requirements for the use of protective equipment. See Parts V and VI of this Chemical Hygiene Plan for further discussion of work situations that require the use of protective equipment.

A. Eye Protection

To minimize the risk of eye injury, MIT policy requires that all personnel, including visitors, wear eye protection at all times while in Chemistry Department laboratories. This eye protection policy is necessary in order that the Institute comply with both Massachusetts and Federal law (e.g. Code of Federal Regulations, Title 29, Section 1910.133). Eye protection is required whether or not one is actually performing a “chemical operation,” and visitors should not be permitted to enter a lab unless they wear appropriate eye protection. Groups that handle chemicals should provide a supply of safety glasses at the entrance of each laboratory for the use of facilities personnel and visitors.

Ordinary **prescription glasses** do not provide adequate protection against injury. **Safety glasses with side shields** provide the minimum protection acceptable for regular use. Safety glasses must meet the American National Standards Institute/International Safety Equipment Association standard ANSI/ISEA Z87.1-2015 which specifies a minimum lens thickness (3 mm), certain impact resistance requirements, etc. Although these safety glasses can provide satisfactory protection against injury from flying particles, they do not fit tightly against the face and offer little protection against splashes or sprays of chemicals. Other eye protection should therefore be employed whenever a significant splash hazard exists (see below).

Contact lenses offer no protection against eye injury and cannot be substituted for safety glasses and goggles. It is best not to wear contact lenses when carrying out operations where a chemical splash to the eyes is possible since contact lenses can interfere with first aid and eye-flushing procedures. If an individual must wear contact lenses for medical reasons, then tight-fitting goggles should be worn over the contact lenses.

Goggles should be worn when carrying out operations in which there is reasonable danger from splashing chemicals, flying particles, etc. For example, goggles are preferred over regular safety glasses when working with glassware under reduced or elevated pressures (e.g. sealed tube reactions), when handling potentially explosive compounds (particularly during distillations), and when employing glass apparatus in high-temperature operations. In some instances “safety shields” should be set up around experiments for additional protection. Since goggles offer little protection to the face and neck, **full-face shields** should be worn when conducting particularly hazardous laboratory operations. In addition, the use of laser or ultraviolet light sources requires special glasses or goggles which have been approved by the Radiation Protection Program.

It is MIT policy to provide prescription safety glasses free of charge to all those personnel working in laboratories who must wear glasses to correct their vision. To obtain prescription safety glasses at MIT’s expense, you must first get a requisition form from Emrick Elias (18-398). Next obtain a prescription (at your own expense) or if you already have a prescription that is less than one year old, this will be sufficient. Take this prescription to MIT Optical (W20-024). Try on and select a pair of frames which are approved by EHS. The optician will take measurements for the frames

and fill out an order form (there is no charge for this). Mail or bring the form to the EHS Office (N52-496). The EHS Office will notify you when your glasses are ready to be picked up. Take the glasses back to MIT Optical so the optician can ensure that the fitting and prescription are correct.

B. Protective Apparel

The choice of protective apparel is determined by the specific hazardous substances being used in an experiment. However, certain general guidelines should be observed at all times in the laboratory:

1. Skin contact with any chemical must always be avoided. Any mixture of chemicals should be assumed to be more toxic than its most toxic component, and substances whose hazards have not been evaluated should be treated as hazardous.
2. As discussed in Parts V and VI, a laboratory coat is required when working with hazardous chemicals, unsealed radioactive materials, and certain biological agents, and when working in areas adjacent to where such hazardous materials are in use. A flame resistant lab coat is required for all work with flammable substances. Flame resistant cotton based coats treated with a flame retardant are acceptable for meeting this requirement, but Nomex lab coats offer increased protection. Nomex coats are required for work with pyrophoric substances, unless the work is performed in a glove box. Exceptions to the requirement for flame resistant lab coats can be approved for certain well defined research such as work with very small quantities of flammable solvents. Requests for such exceptions should be submitted by the PI for the research group to EHS Coordinator, Scott Ide for approval by the EHS Committee. In some cases laboratory supervisors may identify situations where the use of additional more protective apparel is mandatory. A guidance document on “Laboratory Coat Selection, Use, and Care” is available from the Industrial Hygiene Program and can be found at the following url <https://ehs.mit.edu/site/sites/default/files/files/LabCoatGuidance.pdf>.
3. Sandals or open toed shoes should be avoided and long hair and loose clothing should be confined when present in the laboratory. More stringent rules may apply when working with hazardous substances (see Part V-C).
4. Suitable gloves must always be worn when working with hazardous substances. Choose gloves made of material known to be (or tested and found to be) resistant to permeation by the substance in use. A number of different glove selection charts are available on the web to help determine glove permeability. Note that latex gloves provide no protection to exposure to most organic compounds. “4H Gloves,” though expensive, offer the most protection among the various gloves available in Lab Supplies. In some cases two gloves should be worn on each hand to ensure that no exposure will occur in the event of damage to the outer glove. Always inspect gloves for small holes or tears before use. In order to prevent the unintentional spread of hazardous substances, always remove gloves before handling objects such as doorknobs, telephones, pens, etc.

C. Respirators

It is the Institute’s goal to control respiratory hazards at their point of generation by using engineering controls and good work practices. In keeping with this goal, the use of respirators as the primary means of protecting employees from airborne hazards is considered acceptable only in very specific

situations. These situations include short-term temporary experiments where engineering controls are not feasible, and situations in which the use of respiratory protection is an added or supplemental control. A copy of the MIT Respiratory Protection Program is available at <http://ehs.mit.edu/site/content/respiratory-protection>. The following guidelines must be followed when using respirators:

1. Before anyone can wear a respirator, the conditions of the OSHA Standard on Respiratory Protection (29 CFR 1910.134) must be met as discussed below with respect to (a) medical approval, (b) training, and (c) fit testing.
2. Federal regulations require annual medical evaluation of all personnel intending to use a respirator. Appointments for medical evaluations can be arranged by calling the Medical Department at 253-4904. After an examination, the physician will issue a medical approval form which should be taken to the Industrial Hygiene Program where the respirator will be issued.
3. The type of respirator to be used will be selected in consultation with the Industrial Hygiene Program (IHP), N52-496, 452-3477. Respirators can only be purchased through the IHP, and are assigned to individuals for their exclusive use.
4. Personnel must participate in the annual Respirator Training Program prior to using a respiratory device. This training is provided by qualified instructors of the IHP and includes discussion of the proper use, maintenance, testing, cleaning, and storage of respiratory equipment.
5. All users must undergo fit testing (conducted by the Industrial Hygiene Program) when a respirator is first issued and annually as required by OSHA and IHP regulations.
6. The Industrial Hygiene Program (N52-496) will maintain records of respirator users.

The Industrial Hygiene Program will perform annual follow-up reviews of the use of respirators by questionnaire and mandatory fit test. Respirators must be returned to the IHP when no longer needed or when the researcher to whom it was issued leaves MIT.

D. Laboratory Hoods

Local exhaust ventilation is the primary method used to control inhalation exposures to hazardous substances. The laboratory hood is the most common local exhaust method used in the Chemistry Department; other methods include vented enclosures for large pieces of equipment or chemical storage, and snorkel types of exhaust for capturing contaminants near the point of release.

It is advisable to use a laboratory hood when working with all hazardous substances. In addition, a laboratory hood or other suitable containment device must be used for all work with “particularly hazardous substances” (see Part VI). A properly operating and correctly used laboratory hood can control the vapors released from volatile liquids as well as dust and mists.

The fume hoods in the Department of Chemistry are fitted with variable air volume valves. These valves change the exhaust flow rate of the fume hood to maintain a constant face velocity through most of the working range of the sash. The required face velocity depends on the hood type. For most fume hoods fitted with combination sashes (found in Building 18, 2, and 6) the fume hoods are considered to be “high performance” hoods that are designed to operate safely at 80 fpm. Other hoods, such as those fitted only with horizontal sliding sashes (found in Building 6) and vertical only sashes (found in Building 56) the face velocity is set to operate at 100 fpm. The exhaust flow monitor will alarm if a low flow condition exists, if the vertical sash is raised to an unsafe height, or the vertical and horizontal sashes are open on a combination sash. The following rules should be

followed when using laboratory hoods in the Chemistry Department:

1. Do not use a hood when in the low flow alarm condition. No hoods should be used for work involving hazardous substances unless it has a certification label less than one year old.
2. Always keep hazardous chemicals at least six inches behind the plane of the sash.
3. Never put your head inside an operating laboratory hood to check an experiment. The plane of the sash is the barrier between contaminated and uncontaminated air.
4. Work with the hood sash in the lowest possible position. The sash will then act as a physical barrier in the event of an accident in the hood. Effective hood containment is provided with a low sash position even when on low fan mode. Keep the sash closed when not conducting work in the hood. For the combination hoods in Building 18 and 6, keep the horizontal sash closed as much as possible, too. This will not only increase the effectiveness of the hood containment but also save energy and operating costs.
5. Do not clutter your hood with bottles or equipment. Keep it clean and clear. Only materials actively in use should be in the hood. This will provide optimal containment and reduce the risk of extraneous chemicals being involved in any fire or explosion which may occur in the hood.
6. Special rules for horizontal sashes. Keep the bottom sash track for horizontal panels free of debris so the sashes can be closed quickly in the event of an incident. Electrical cords for equipment must be fed under the hood airfoil not through the horizontal sash opening to allow for vertical and horizontal panel movement.
7. Clean the grill along the bottom slot of the hood regularly so it does not become clogged with papers and dirt.
8. Any modifications to the hoods, specialty local exhaust or duct work require the approval of the EHS Industrial Hygiene Program (452-3477).
9. Do not place large pieces of equipment inside the lab fume hood unless the hood is dedicated to this use (large obstructions can change the airflow patterns and render the hood unsafe for other uses). It is generally more effective to install a specifically designed enclosure for large equipment so that the laboratory hood can be used for its intended purpose.
10. Promptly report any suspected hood malfunctions to the Industrial Hygiene Program (452-3477).

Further discussion of the proper use of laboratory hoods can be found in the following references:

Prudent Practices in the Laboratory: Handling and Disposing of Chemicals, National Academy Press, 1995, pp. 178-195

Prudent Practices in the Laboratory: Handling and Management of Chemical Hazards, National Academies Press, 2011, pp. 221-234.

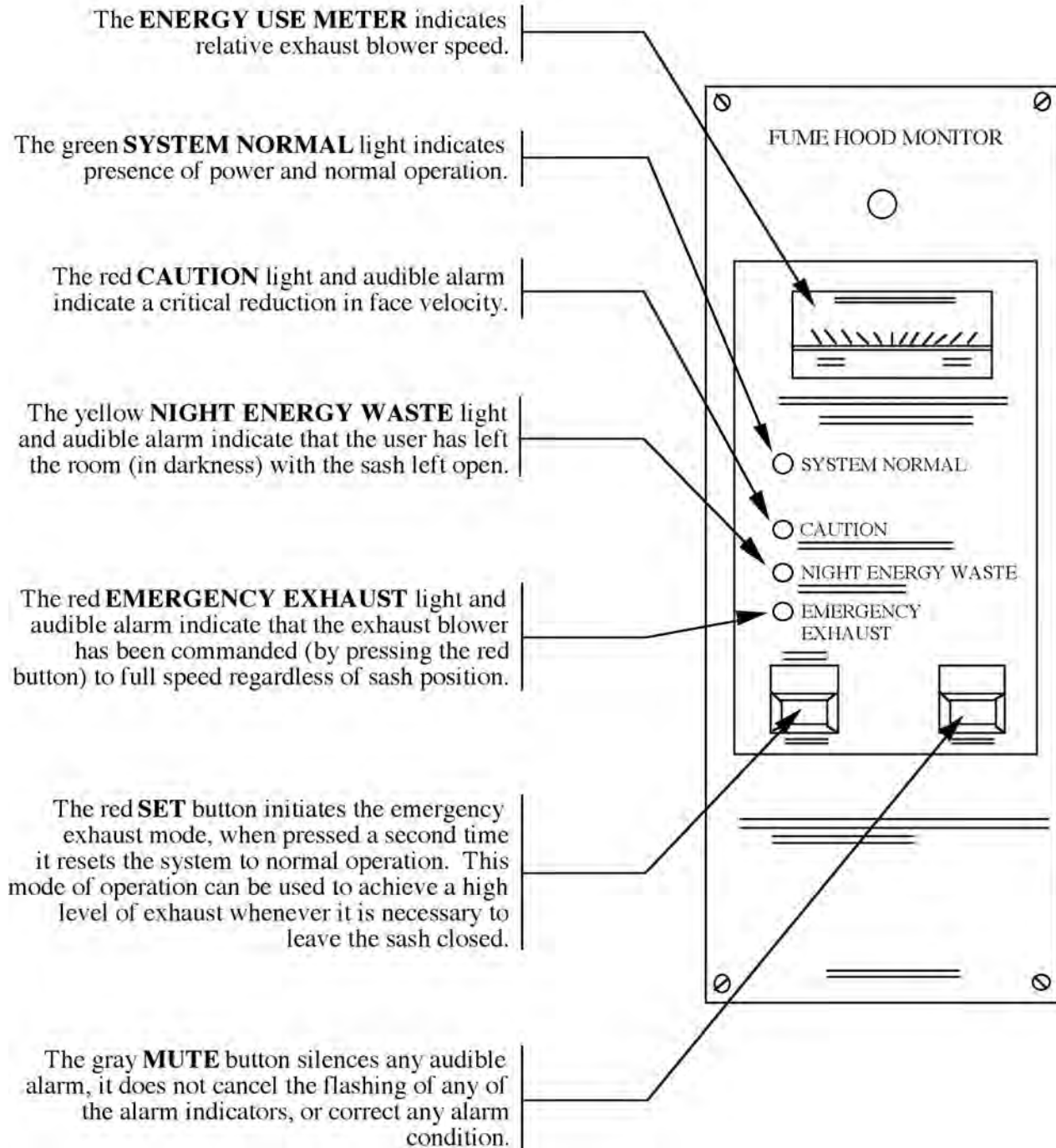
Improving Safety in the Chemical Laboratory, Young, J. A. Ed., Wiley, 1987, pp. 287-319.

Mikell, W. G.; Drinkard, W. C. "Good Practices for Hood Use," *J. Chem. Ed.* 1984, 61, A13.

Mikell, W. G.; Fuller, F. H. "Good Hood Practices for Safe Hood Operation," *J. Chem. Ed.* 1988, 65, A36.

FUME HOOD MONITOR

The fume hood monitor provides the user with the status of system operation and enables user intervention. It translates the sash position, via the sash sensor, and commands the variable air valve to regulate the exhaust flow rate in order to maintain a constant sash face velocity.



E. Fire Extinguishers, Safety Showers, and Eyewash Facilities

Laboratory supervisors are required to instruct new personnel in the location of fire extinguishers, safety showers, and eyewashes before they begin research in the laboratory. It is MIT policy that personnel are not required to extinguish fires that occur in their work areas. However, as discussed in Part V, under certain circumstances properly trained personnel may attempt to extinguish fires. Researchers are not permitted to use fire extinguishers unless they have attended a Fire Extinguisher Training Session presented by the MIT EHS Office. Contact Scott Ide, EHS Coordinator (324-6132) for information on the schedule of fire extinguisher training sessions.

All laboratories in the Chemistry Department are provided with fire extinguishers. All fire extinguishers should be mounted on a wall in an area free of clutter or stored in a fire extinguisher cabinet. Research personnel should be familiar with the location, use, and classification of the extinguishers in their laboratory. The types of extinguishers are described below, as well as their classification and suitability for use with different types of fires.

1. **Carbon dioxide extinguishers** are effective against Class B fires, (involving burning liquids such as solvents) and Class C electrical fires. They are not as effective against burning paper or trash fires. Do not use a CO₂ extinguisher against fires involving alkali and certain other metals (such as Al, Mg, and Zn) and compounds such as lithium aluminum hydride.
2. **Dry powder extinguishers** can also be used against Class B and C fires (burning liquids and electrical fires). These extinguishers contain sodium bicarbonate and are not recommended for fires involving delicate instruments or optical systems.
3. **Water extinguishers** should only be used for Class A (paper and trash) fires. The use of water against electrical, liquid, and metal fires is not recommended and can intensify or spread the fire instead of extinguishing it.
4. **Met-L-X and Met-L-Kyl**. These materials are effective against burning metals including magnesium, lithium, sodium, potassium, reactive metal alloys, metal hydrides, metal alkyls, and other organometallic compounds (Class D fires).
5. **Sand** can be used on any type of fire (Class A, B, C, or D) and is especially useful against small Class D (metal) fires.

Any time a fire extinguisher is used, no matter for how brief a period, it should be inspected and recharged. For recharging, replacement, inspection, or information regarding the type of extinguisher best suited for your laboratory, call the MIT Operations Center at x3-1500. It is the responsibility of Group EHS Representatives in their capacity as Group Fire Wardens to inspect the portable fire extinguishers, safety showers, and eyewash facilities in their laboratories once each month. Every laboratory in the Department in which hazardous substances are in use must be equipped with an unobstructed **safety shower** and **eyewash facility** that meets the requirements of OSHA regulations (29 CFR 1910.151(c)). Fire extinguishers are inspected and tagged annually by the Facilities Department. Safety showers are also inspected once each year. Eyewashes are no longer inspected by Facilities. EHS Representatives are required to flush the eyewash stations on a weekly basis. This will flush out any bacteria that grow in the stagnant water. If an eyewash or safety shower needs to be repaired, call x 3-1500 and give the operator the location of the defective equipment and (for safety showers) the number on the blue preventive maintenance tag. In addition to the inspections performed by the Safety Program, the Chemistry Department EHS Committee also holds laboratory safety inspections several times each year. These inspections are usually unannounced and include the inspection of all safety equipment, such as fire extinguishers, safety showers, eyewashes, and fire blankets.

Part V. Standard Operating Procedures for Working with Hazardous Substances

A. Classes of Hazardous Substances

Many of the substances encountered in the laboratory are known to be toxic or corrosive, or both. Compounds that are explosive and/or are highly flammable pose another significant type of hazard. New and untested substances that may be hazardous are also frequently encountered. Thus, it is essential that all laboratory workers understand the types of toxicity, recognize the routes of exposure, and are familiar with the major classes of toxic and corrosive chemicals. The most important single generalization regarding toxicity in chemical research is *treat all compounds as potentially harmful, especially new and unfamiliar materials, and work with them under conditions to minimize exposure by skin contact and inhalation.*

When considering possible toxicity hazards while planning an experiment, it is important to recognize that the combination of the toxic effects of two substances may be significantly greater than the toxic effect of either substance alone. Because most chemical reactions are likely to contain mixtures of substances whose combined toxicities have never been evaluated, it is prudent to assume that mixtures of different substances (e.g., chemical reaction mixtures) will be more toxic than the most toxic ingredient contained in the mixture. Furthermore, chemical reactions involving two or more substances may form reaction products that are significantly more toxic than the starting reactants.

The OSHA Laboratory standard (29 CFR 1910.1450) defines a hazardous substance as “*a chemical for which there is statistically significant evidence based on at least one study conducted in accordance with established scientific principles that acute or chronic health effects may occur in exposed employees. The term ‘health hazard’ includes chemicals which are carcinogens, toxic or highly toxic agents, reproductive toxins, irritants, corrosives, sensitizers, hepatotoxins, nephrotoxins, neurotoxins, agents which act on the hematopoietic systems, and agents which damage the lungs, skin, eyes, or mucous membranes.*” Highly flammable and explosive substances comprise another category of hazardous compounds. The major classes of hazardous substances are discussed in further detail below.

(1) Carcinogens

Carcinogens are chemical or physical agents that cause cancer. Generally they are chronically toxic substances; that is, they cause damage after repeated or long-duration exposure, and their effects may only become evident after a long latency period. Chronic toxins are particularly insidious because they may have no immediate apparent harmful effects.

Certain *select carcinogens* are classified as “particularly hazardous substances” and must be handled using the special precautions described in Part VI. Select carcinogens (defined in detail in Part VI-A) include compounds for which there is evidence from human studies that exposure can cause cancer. For a large number of other compounds there is limited evidence of carcinogenicity from studies involving experimental animals. These compounds should be handled using the general procedures for work with hazardous substances outlined in Part V below.

It is important to recognize that many of the substances involved in research in Chemistry Department laboratories are new compounds and have not been subjected to testing for carcinogenicity. Researchers should therefore be familiar with the specific classes of compounds and functional group

types that have previously been correlated with carcinogenic activity. The following discussion provides an introduction to this subject and lists representative compounds in each class that are “reasonably anticipated to be carcinogens” based on animal tests. Always keep in mind that as a general rule, all new and untested compounds should be regarded as being toxic substances.

Classes of Carcinogenic Compounds (**select carcinogens*)

Alkylating agents: α -halo ethers

- **bis(chloromethyl)ether*
- **methyl chloromethyl ether*

Alkylating agents: sulfonates

- **1,4-butanediol dimethanesulfonate*
- diethyl sulfate
- dimethyl sulfate
- ethyl methanesulfonate
- methyl methanesulfonate
- methyl trifluoromethanesulfonate
- 1,3-propanesultone

Alkylating agents: epoxides

- *ethylene oxide
- diepoxybutane
- epichlorohydrin
- propylene oxide
- styrene oxide

Alkylating agents: aziridines

- **ethylenimine*
- 2-methylaziridine

Alkylating agents: diazo, azo, and azoxy compounds

- 4-dimethylaminoazobenzene

Alkylating agents: electrophilic alkenes and alkynes

- **acrylonitrile*
- acrolein
- ethyl acrylate

Acylation agents

- * β -*propiolactone*
- β -butyrolactone
- dimethylcarbamoyl chloride

Organohalogen compounds

- **1,2-dibromo-3-chloropropane*
- **mustard gas (bis(2-chloroethyl)sulfide)*
- **vinyl chloride*
- carbon tetrachloride
- chloroform
- 3-chloro-2-methylpropene
- 1,2-dibromoethane
- 1,4-dichlorobenzene
- 1,2-dichloroethane
- 2,2-dichloroethane
- 1,3-dichloropropene
- hexachlorobenzene
- methyl iodide
- tetrachloroethylene
- trichloroethylene
- 2,4,6-trichlorophenol

Hydrazines

- **hydrazine* (and hydrazine salts)
- 1,2-diethylhydrazine
- 1,1-dimethylhydrazine
- 1,2-dimethylhydrazine

N-nitroso compounds

- **N-nitrosodimethylamine*
- N-nitroso-N-alkylureas

Aromatic amines

- **4-aminobiphenyl*
- **benzidine (p,p'-diaminobiphenyl)*
- * α -*naphthylamine*
- * β -*naphthylamine*
- aniline
- o*-anisidine (2-methoxyaniline)
- 2,4-diaminotoluene
- o*-toluidine

Aromatic hydrocarbons

*benzene
benz[a]anthracene
benzo[a]pyrene

Natural products (including antitumor drugs)

adriamycin
aflatoxins
bleomycin
cisplatin
progesterone
reserpine
safrole

Miscellaneous organic compounds

*formaldehyde (gas)
acetaldehyde
1,4-dioxane
ethyl carbamate (urethane)
hexamethylphosphoramide
2-nitropropane
styrene
thiourea
thioacetamide

Miscellaneous inorganic compounds

*arsenic and certain arsenic compounds
*chromium and certain chromium compounds
*thorium dioxide
beryllium and certain beryllium compounds
cadmium and certain cadmium compounds
lead and certain lead compounds
nickel and certain nickel compounds
selenium sulfide

The preceding compounds were selected from lists of substances identified as carcinogens or potential carcinogens by OSHA, the International Agency for Research on Cancer (IARC), and the Annual Report on Carcinogens published by the National Toxicology Program (NTP). References in the Library of Lab Safety and the Industrial Hygiene Program (2-3477) should be consulted for additional information.

When evaluating the carcinogenic potential of chemicals, it should be noted that exposure to certain combinations of compounds (not necessarily simultaneously) can cause cancer even at exposure levels where neither of the individual compounds would have been carcinogenic. 1,8,9-Trihydroxyanthracene and certain phorbol esters are examples of “*tumor promoters*” that while not themselves carcinogenic, can dramatically amplify the carcinogenicity of other compounds.

(2) Reproductive and Developmental Toxins

Reproductive toxins are substances that have adverse effects on various aspects of reproduction including fertility, gestation, lactation, and general reproductive performance. *Developmental* toxins are substances that act during pregnancy to cause adverse effects on the embryo or fetus. These effects can include lethality (death of the fertilized egg, the embryo, or the fetus), malformations (this class of substances is also called teratogens), retarded growth, and postnatal functional deficiencies. When a pregnant woman is exposed to a chemical, generally the fetus is exposed as well since the placenta is an extremely poor barrier to chemicals. It is important to understand that reproductive toxins can affect both men and women. Male reproductive toxins can in some cases lead to sterility. Two well known male reproductive toxins are ethylene dibromide and dibromochloropropane. Many

reproductive toxins are chronic toxins which cause damage after repeated or long-duration exposures with effects that become evident only after long latency periods.

Information on reproductive toxins can be obtained from Safety Data Sheets, by contacting the Industrial Hygiene Program (2-3477), and by consulting the *Catalog of Teratogenic Agents*, Sixth Edition; Shepard, T. H.; Johns Hopkins University Press, Baltimore, 1989. Also see Beyler, R. E. and Meyers, V. K. *J. Chem. Ed.* 1982, 59, 759-763 for a discussion of “What Every Chemist Should Know About Teratogens.” The following Table lists some common materials that are highly suspected to be reproductive toxins.

Partial List of Reproductive Toxins

arsenic and certain arsenic compounds	ethylene oxide
benzene	lead compounds
cadmium and certain cadmium compounds	mercury compounds
carbon disulfide	toluene
ethylene glycol monomethyl and ethyl ethers	vinyl chloride
	xylene

The above list is not intended to be complete, and it is the responsibility of the researcher and their laboratory supervisor to evaluate each compound involved in their work and to determine whether it should be handled as a reproductive toxin.

The period of greatest susceptibility to embryotoxins is the first 8-12 weeks of pregnancy, a period which includes time when a woman may not know she is pregnant. Consequently, women of child-bearing potential should take care to avoid all skin contact with chemicals. Pregnant women and women intending to become pregnant should consult with their personal physician, their laboratory supervisor and the Industrial Hygiene Program with regard to the type of work they may safely perform and the special precautions they should take. The contact in the Industrial Hygiene Program is Robert Edwards (3-9391). All consultations are kept in strict confidence.

(3) Corrosive Substances

Corrosive substances cause visible destruction of, or visible alterations in, living tissue by chemical action at the site of contact. Major classes of corrosive substances include strong acids (e.g., sulfuric, nitric, hydrochloric, and hydrofluoric acids), strong bases (sodium hydroxide, potassium hydroxide, and ammonium hydroxide), dehydrating agents (sulfuric acid, sodium hydroxide, phosphorus pentoxide, and calcium oxide), and oxidizing agents (hydrogen peroxide, chlorine, and bromine).

(4) Irritants

Irritants are defined as non-corrosive chemicals that cause reversible inflammatory effects on living tissue by chemical action at the site of contact. A wide variety of organic and inorganic compounds are irritants and consequently skin contact with all laboratory chemicals should always be avoided.

(5) Toxic and Highly Toxic Agents

OSHA regulations (29 CFR 1910.1200 Appendix A) define toxic and highly toxic agents as substances with median lethal dose (LD50) values in the following ranges:

Oral LD50 (albino rats)	<i>Toxic</i> 50-500 mg/kg	<i>Highly Toxic</i> <50 mg/kg
Skin Contact LD50 (albino rabbits)	200-1000 mg/kg	<200 mg/kg
Inhalation LC50 (albino rats)	200-2000 ppm/air	<200 ppm/air

It is important to note that the above classification does not take into consideration chronic toxicity (i.e. carcinogenicity and reproductive toxicity). Also, note that LD50 values vary significantly between different species, and the human toxicity for a substance may be greater or less than that measured in test animals.

In evaluating the **acute toxicity** of chemical substances, the **HMIS** (Hazardous Materials Identification System) rating criteria developed by the National Paint and Coatings Association may be helpful. HMIS numbers can often be found in SDS's. LD50 values can be found in SDS's and in references such as the *Sigma-Aldrich Library of Chemical Safety Data* and Patnaik's *A Comprehensive Guide to the Hazardous Properties of Chemical Substances*.

Hazard Level	HMIS #	Rating	Oral LD50 (Rats, per kg)	Skin Contact LD50 (Rabbits, per kg)	Inhalation (ppm for 1 h)	ILC50 (Rats) (mg/m ³ for 1 h)
HIGH (Poison)	4	Extremely toxic	<1 mg	<20 mg	<20	<200
	3	Highly toxic	1-50 mg	20 - 200 mg	20-200	200-2000
MEDIUM (Harmful)	2	Moderately toxic	50-500 mg	200 mg-1 g	200-2,000	2000-20,000
LOW	1	Slightly toxic	500 mg-5 g	1-5 g	2,000-20,000	20,000-200,000
	0	Practically non-toxic	>5 g	>5 g	>20,000	>200,000

(6) Hazardous Substances with Toxic Effects on Specific Organs

Substances included in this category include (a) hepatotoxins (substances that produce liver damage such as nitrosamines and carbon tetrachloride); (b) nephrotoxins (agents causing damage to the kidneys such as certain halogenated hydrocarbons), (c) neurotoxins (substances which produce their primary toxic effects on the nervous system such as mercury, acrylamide, and carbon disulfide), (d) agents which act on the hematopoietic system (such as carbon monoxide and cyanides which decrease hemoglobin function and deprive the body tissues of oxygen), and (e) agents which damage lung tissue such as asbestos and silica.

(7) Sensitizers

A sensitizer (allergen) is a substance that causes exposed people to develop an allergic reaction in normal tissue after repeated exposure to the substance. Examples of allergens include diazomethane, chromium, nickel, formaldehyde, isocyanates, arylhydrazines, benzylic and allylic halides, peptide coupling reagents such as HATU and HBTU, as well as many phenol derivatives.

(8) Flammable and Explosive Substances

A number of highly flammable substances are in common use in Chemistry Department laboratories. Explosive substances are materials that decompose under conditions of mechanical shock, elevated temperature, or chemical action, with the release of large volumes of gases and heat.

B. Risk Assessment for Hazardous Substances

The following outline provides a summary of the steps that laboratory workers should use to assess the risks of handling hazardous chemicals. Note that if a Laboratory Chemical Safety Summary is not already available, then following the protocol outlined here should enable a worker to prepare their own LCSS. For a detailed discussion of how to evaluate hazards and assess risks in the laboratory, see Chapter 4 of *Prudent Practices in the Laboratory: Handling and Management of Chemical Hazards*, National Academies Press, 2011.

It is the responsibility of researchers to make a determination as to whether they have sufficient knowledge and experience to carry out an experiment safely. This is a necessary step in the risk assessment performed prior to carrying out every experiment. If a researcher has any doubt as to whether they understand the proper procedures to carry out an experiment safely, they should not proceed and should seek advice from their laboratory supervisor, their EHS Coordinator (Scott Ide), and/or the EHS Office.”

(1) **Identify chemicals to be used and circumstances of use.** Identify the chemicals involved in the proposed experiment and determine the amounts that will be used. Is the experiment to be done once, or will the chemicals be handled repeatedly? Will the experiment be conducted in an open laboratory, in an enclosed apparatus, or in a fume hood? Is it possible that new or unknown substances will be generated in the experiment? Are any of the workers involved in the experiment pregnant or likely to become pregnant? Do they have any known sensitivities to specific chemicals?

(2) **Consult sources of information.** Consult an up-to-date LCSS for each chemical involved in the planned experiment (examine an up-to-date SDS if an LCSS is not available). In cases where substances with significant or unusual potential hazards are involved, it may also be advisable to consult additional more detailed references such as NIOSH/OSHA Guidelines, Patnaik, Patty’s, and other sources discussed in Part III-B above. Depending on the researcher’s level of experience and the degree of potential hazard associated with the proposed experiment, it may also be necessary to obtain the assistance of supervisors and safety professionals before proceeding with risk assessment.

(3) **Evaluate type of toxicity.** Use the above sources of information to determine the type of toxicity associated with each chemical involved in the proposed experiment. Are any of the chemicals to be used acutely toxic or corrosive? Are any of the chemicals to be used irritants or sensitizers? Will any select carcinogens or possibly carcinogenic substances be encountered? For many

substances, it will be necessary to consult the listings of carcinogens in Part V-A to identify chemical similarities to known carcinogens. Are any chemicals involved in the proposed experiment suspected to be reproductive or developmental toxins, or neurotoxins?

(4) **Consider possible routes of exposure.** Determine the potential routes of exposure for each chemical. Are the chemicals gases, or are they volatile enough to present a significant risk of exposure through inhalation? If liquid, can the substances be absorbed through the skin? Is it possible that dusts or aerosols will be formed in the experiment? Does the experiment involve a significant risk of inadvertent ingestion or injection of chemicals?

(5) **Evaluate quantitative information on toxicity.** Consult the information sources to determine the LD50 for each chemical via the relevant routes of exposure. Determine the acute toxicity hazard level for each substance, classifying each chemical as highly toxic, moderately toxic, slightly toxic, etc. For substances which pose inhalation hazards, take note of the TLV-TWA, STEL, and PEL values.

(6) **Select appropriate procedures to minimize exposure.** All work involving chemicals in MIT Chemistry Department laboratories should be conducted using the “General Procedures for Work with Toxic Substances” described in the next section of this Chemical Hygiene Plan. In addition, laboratory workers must determine whether any of the chemicals to be handled in the planned experiment meet the definition of a *particularly hazardous substance* due to high acute toxicity, carcinogenicity, and/or reproductive toxicity. If so, consider the total amount of the substance that will be used, the expected frequency of use, the chemical’s routes of exposure, and the circumstances of its use in the proposed experiment. Use this information to determine whether it is appropriate to apply the additional “Procedures for Work with Particularly Hazardous Substances” outlined in Part VI. For very toxic substances, consider whether additional consultation with safety professionals is warranted.

(7) **Evaluate hazards due to flammable and explosive substances.** It should be noted that the risk assessment procedures described so far in this section address only the hazards due to the toxic effects of chemicals. Hazards due to flammability, explosion, and reactivity are equally important in risk assessment, and are discussed in Section D of this Part of the Chemical Hygiene Plan. Sources of information should be consulted to evaluate the flammability, reactivity, and explosability of each chemical involved in the proposed experiment, and appropriate steps to minimize risks should then be taken as outlined below in Section V-D.

(8) **Prepare for contingencies.** Note the signs and symptoms of exposure to the chemicals to be used in the proposed experiment. Note appropriate measures to be taken in the event of exposure or accidental release of any of the chemicals, and in the event of a fire.

C. General Procedures for Working with Toxic Substances

Literally thousands of different compounds are involved in the research being conducted in Chemistry Department laboratories. The specific health hazards associated with many of these compounds are unknown, and many substances are new compounds which have not been reported previously in the chemical literature. Consequently it is impossible in this Chemical Hygiene Plan to provide standard operating procedures for specific hazardous substances. Instead, this section outlines general procedures which should be employed in the use of all hazardous substances. Individual research groups may wish to supplement these general procedures with standard operating procedures for handling specific hazardous substances that are in frequent use in their laboratories.

Several general principles apply to all work conducted in the Chemistry Department laboratories involving hazardous substances.

1. **Preparation.** A cardinal rule of laboratory research is that workers must determine the potential hazards associated with an experiment before beginning it. *Before working with any chemical, it is the responsibility of the researcher to determine what physical and health hazards are associated with the substance.* This determination may require consulting library references and safety data sheets, and may involve discussions with the laboratory supervisor and Industrial Hygiene Program.
2. **Minimize exposure to chemicals.** All skin contact with chemicals in the laboratory should be avoided. Use laboratory hoods and other ventilation devices to prevent exposure to airborne substances whenever possible (note that the use of hoods is **required** for work with many hazardous substances).
3. **Do not underestimate risks.** Assume that any mixture of chemicals will be more toxic than its most toxic component. All new compounds and substances of unknown toxicity should be treated as toxic substances.
4. **Be prepared for accidents.** Before beginning an experiment, know what specific action you will take in the event of the accidental release of any hazardous substances involved. Know the location of all safety equipment including fire extinguishers, fire blankets, eye washes, safety showers, spill carts and spill control materials, be familiar with the location of the nearest fire alarm and telephone, and know what telephone numbers to call in the event of an emergency. Know the location of the circuit breakers for your laboratory.

It should be evident from the discussion in Part V-A above that the majority of chemicals involved in research in Chemistry Department laboratories must be considered to be “hazardous substances.” In addition to the four general principles outlined above, the following procedures should be standard practice for all work involving the use of hazardous substances.

(1) Eye Protection

MIT policy requires that all personnel, including visitors, wear eye protection at all times while in Chemistry Department laboratories. Eye protection is discussed in detail in Part IV-A of this Chemical Hygiene Plan.

(2) Personal Apparel

Do not wear sandals or open-toed shoes or shoes made of woven material when working with hazardous substances. Confine long hair and loose clothing. Use suitable protective apparel including gloves as discussed in detail in Part IV-B. Full length pants, or the equivalent is required when working with hazardous chemicals, unsealed radioactive materials, and certain biological agents, and when working in areas adjacent to where such hazardous materials are in use. Also, the area of skin between the shoe and ankle should not be exposed. A laboratory coat is required when working with hazardous chemicals, unsealed radioactive materials, and certain biological agents, and when working in areas adjacent to where such hazardous materials are in use. A flame resistant lab coat is required for all work with flammable substances. Flame resistant cotton based coats treated with a flame retardant are acceptable for meeting this requirement, but Nomex lab coats offer increased protection. Nomex coats are required for work with pyrophoric substances, unless the work is performed in a glove box.

Exceptions to the requirement for flame resistant lab coats and long pants can be approved for certain

well defined research such as work with very small quantities of flammable solvents. Requests for such exceptions should be submitted by the PI for the research group to EHS Coordinator, Scott Ide (scottide@mit.edu) for approval by the EHS Committee. In some cases laboratory supervisors may identify situations where the use of additional more protective apparel is mandatory.

(3) Avoid Skin Contact and Ingestion of Hazardous Substances

Contact with the skin is a frequent mode of chemical injury. A common result of skin contact is localized irritation, but an appreciable number of hazardous substances are absorbed through the skin with sufficient rapidity to produce systemic poisoning. Avoid contact with hazardous substances by taking the following precautions:

- (a) Wear gloves that are not permeable to the hazardous substances being used.
- (b) Never use mouth suction to pipet chemicals or to start a siphon; a pipet bulb or aspirator should instead be used to provide vacuum.
- (c) Never taste laboratory chemicals.
- (d) Wash your hands with soap and water immediately after working with hazardous chemicals.
- (e) Eating, drinking, smoking, gum-chewing, and applying cosmetics in laboratories where hazardous substances are in use is prohibited by Federal law. Do not store food, beverages, cups, or other drinking and eating utensils in areas where hazardous chemicals are used or stored.

(4) Avoid Inhalation of Toxic Substances

Inhalation of toxic vapors, mists, gases, or dusts can produce poisoning by absorption through the mucous membranes of the mouth, throat, and lungs, and can seriously damage these tissues by local action. Inhaled gases or vapors may pass rapidly into the capillaries of the lungs and be carried into the circulatory system. This absorption can be extremely rapid. Procedures involving volatile toxic substances and those operations involving solid or liquid toxic substances that may result in the generation of aerosols should be conducted in a laboratory hood or other containment device. See Part IV-C for a detailed discussion of laboratory hoods. OSHA Permissible Exposure Limits (PELs) and American Conference of Governmental Industrial Hygienists Threshold Limit Values (TLVs) should be observed when working with hazardous substances for which PELs and TLVs have been established (see the ACGIH booklet in the Library of Lab Safety for tables of TLV values of laboratory chemicals). Never smell compounds of unknown toxicity.

(5) Use and Maintenance of Equipment and Glassware

Good equipment maintenance is important for safe, efficient operations. Equipment should be inspected and maintained regularly. Servicing schedules will depend on both the possibilities and the consequences of failure. Maintenance plans should include a procedure to ensure that a device that is out of service cannot be restarted.

Improper use of glassware is a frequent cause of injuries and accidents in the laboratory.

- (a) Careful handling and storage procedures should be used to avoid damaging glassware. Always carefully inspect glassware for flaws and cracks before use. Damaged items should be discarded or repaired.
- (b) Adequate hand protection should be used when inserting glass tubing into rubber stoppers or corks or when placing rubber tubing on glasshose connections. Tubing should be fire polished or rounded and lubricated, and hands should be held close together to limit movement of glass should fracture occur. The use of plastic or metal connectors should be considered.

- (c) Glass-blowing operations should not be attempted unless proper annealing facilities are available.
- (d) Vacuum-jacketed glass apparatus should be handled with extreme care to prevent implosions. Equipment such as Dewar flasks should be taped or shielded. Only glassware designed for vacuum work should be used for that purpose.
- (e) Hand protection should be used when picking up broken glass. (Small pieces should be swept up with a brush into a dustpan).
- (f) Broken glassware, syringes, and other “sharp objects” must be disposed of properly. Such waste should be separated from other trash and stored for pickup in clearly marked containers labeled “sharps.”

(6) Housekeeping

There is a definite relationship between safety and orderliness in the laboratory. The following housekeeping rules should be adhered to in all laboratories:

- (a) Work areas (including floors) should be cleaned regularly. Do not allow trash to accumulate.
- (b) Access to exits and safety equipment must not be obstructed.
- (c) All gas tanks should be secured to walls or benches.
- (d) Solvents should not be stored on the floor and large containers (more than 1 liter) must be stored below eye level (e.g. in cabinets).
- (e) Chemical storage refrigerators should be defrosted periodically and should not be overcrowded.
- (f) Acid and base baths in 5 gallon pails should not be stored on bench-tops since they can easily tip over.

(7) Working Alone Policy

Researchers should avoid working alone with hazardous materials or equipment or otherwise working under conditions that may create the risk of serious injury (hereafter referred to as hazardous conditions). Working alone means when no one else is in direct line of sight or within sound of the person. Anyone at MIT (faculty, staff, students, and visitors) who works under (or intends to work under) potentially hazardous conditions that may result in immediate injury or serious harm must discuss this activity with their Principal Investigator (PI) or faculty supervisor prior to conducting the work alone and determine that the risk of working alone is controllable under the specific conditions established by the PI or supervisor for the work. If the PI or faculty supervisor determines that the risk cannot be minimized to a controllable level, then the individual should perform the work only when others are present or a suitable alarm device is available that will summon help immediately.

Undergraduates shall not work alone with hazardous materials, equipment, or operations that can result in immediate injury or death without prior written approval from the immediate PI or supervisor. Written approval should only be granted after a risk assessment is performed and reviewed by the PI with the undergraduate student.

(8) Work Conducted Outside Normal Hours

Laboratory operations involving hazardous substances are sometimes carried out continuously or overnight. It is the responsibility of the researcher to design these experiments with provisions to prevent the release of hazardous substances in the event of interruptions in utility services such as electricity, cooling water, and inert gas. Laboratory lights should be left on and appropriate signs should be posted identifying the nature of the experiment and the hazardous substances in use. In some cases arrangements should be made for periodic inspection of the operation by other workers. Information should be left indicating how to contact you in the event of an emergency.

(9) Children and Pets in Laboratories

Pets such as dogs are not permitted in laboratories where hazardous substances are stored or are in use. Children are only permitted in department laboratories for brief periods of time and while under the direct supervision of their parent or other qualified adult.

(10) Storage of Hazardous Substances

Researchers should refer to *Prudent Practices in the Laboratory: Handling and Management of Chemical Hazards*, National Academies Press 2011, pp. 94–101 for a discussion of procedures for storing chemicals in laboratories. All procedures employed must comply with OSHA regulations.

- (a) Access to all hazardous chemicals, including toxic and corrosive substances, should be restricted at all times. Specifically, these materials should be stored in laboratories that are kept locked at all times that laboratory personnel are not present. An additional level of security is required for unusually toxic and hazardous chemicals, which should be stored within laboratories in locked storerooms or locked storage cabinets.
- (b) To avoid the accumulation of excess chemicals, always purchase the minimum quantities of commercial chemicals necessary for your research.
- (c) All containers of chemicals (including research samples) should be properly labeled. When appropriate, special hazards should be indicated on the label. For certain classes of compounds (e.g. ethers), the date the container was opened should be written on the label.
- (d) Only small quantities (less than or equal to 1 liter) of flammable liquids should be kept at work benches. Larger quantities should be stored away from ignition sources in ventilated steel storage cabinets or fume hoods. It is advisable to purchase highly flammable solvents (e.g., acetone, hexane, diethyl ether, ethyl acetate, THF) only in metal or break-resistant (i.e., plastic or plastic-coated) containers.
- (e) Refrigerators used for storage of chemicals must be explosion-proof or laboratory-safe type units. Storage trays or secondary containers should be used to minimize the distribution of material in the event a container should leak or break. Volatile chemicals that are flammable and/or toxic should not be stored in walk-in cold rooms.
- (f) Large containers (more than 1 liter) should be stored below eye-level on low shelves. Never store hazardous chemicals on the floor.
- (g) Research groups must maintain an inventory list or card file of hazardous substances present in their laboratories. The use of Environmental Health & Safety Assistant (EHSA) inventory system is recommended, but not required. For more information on Environmental Health & Safety Assistant (EHSA), please contact the EHS Office by filling out the online request form (<https://ehs.mit.edu/site/content/inventory-user-request-form>) or by calling 2-3477.

For a further discussion of safe chemical storage, see Pipetone, D. A.; Hedberg, D. D. *J. Chem. Ed.* 1982, 59, A159.

(11) Transporting Hazardous Substances

MIT policy requires that any chemicals that are transported outside of a laboratory carried in approved secondary containers. Approved secondary containers are defined as commercially available bottle carriers made of rubber, metal, or plastic, with carrying handle(s), and which are large enough to hold

the contents of the chemical container in the event of breakage. It is advisable to use the stairwells whenever possible, in lieu of the elevator, for transporting hazardous substances. When transporting cylinders of compressed gases, always strap the cylinder in a suitable hand truck and protect the valve with a cover cap. See the MIT EHS Office webpage for more information on compressed gas cylinders, <https://ehs.mit.edu/site/laboratory-safety/compressed-gas-cylinder-safety>.

Because of the potential suffocation risk associated with liquid nitrogen, Chemistry Department personnel are not permitted to accompany dewars of liquid nitrogen on elevators. To transport liquid nitrogen on elevators, one researcher will load the liquid nitrogen dewar onto an empty elevator and send it to the floor where another group member awaits to receive it. The dewars shall have laminated signs warning people not to enter the elevator (in case it stops at an intervening floor). When loading a dewar onto an elevator for transport, researchers shall orientate the dewar toward the front of the elevator with the warning sign clearly visible. Dewars also need to be labeled with the appropriate group name and room number in order to minimize the risk of being lost.

(12) Handling of Excess and Waste Chemicals

Consideration of the means of disposal of chemical wastes should be part of the planning of all experiments *before they are carried out*. The cost of disposing of excess and waste chemicals has become extremely expensive, and frequently exceeds the original cost of purchasing the chemical. Whenever practical, order the minimum amount of material possible in order to avoid the accumulation of large stocks of “excess chemicals” which will not be needed in future research. Such collections of “excess chemicals” frequently constitute safety hazards, since many substances decompose upon long storage and occasionally their containers become damaged or degrade. In addition, the disposal of significant quantities of excess chemicals ultimately presents a very significant financial burden to faculty research accounts.

Outline of Procedures for Handling Excess and Waste Chemicals

This section presents specific procedures for handling the most common classes of excess and waste chemicals. It is the responsibility of the individual researcher (with the assistance of their faculty supervisor) to evaluate the properties of the excess and waste chemicals resulting from their work, and to determine when special handling procedures are needed outside the general guidelines outlined below. The MIT Environmental Management Program (2-3477) should be consulted for assistance in planning the disposal of such hazardous compounds. In some cases the further chemical transformation of reaction byproducts is advisable as an integral part of an experimental procedure. In this connection, detailed procedures for the laboratory transformation of a number of hazardous chemicals can be found in Chapter 7 of *Prudent Practices in the Laboratory: Handling and Disposing of Chemicals*, National Academy Press, 1995 edition and in the reference *Destruction of Hazardous Chemicals in the Laboratory* by G. Lunn and E. B. Sansone (copy available in the Department Library of Lab Safety).

(a) Definition of Hazardous Chemical Waste

- See Chapter 8 of *Prudent Practices in the Laboratory: Handling and Management of Chemical Hazards*, National Academies Press, 2011, concerning chemical hazardous waste. The term “hazardous waste” is defined as any material that possesses hazardous characteristics (e.g., that is toxic, ignitable, corrosive, or reactive), or is listed as hazardous waste by the regulatory agencies.

- Note that materials associated with “experiments in progress” are not classified as waste.
- Speculative accumulations of chemicals can be classified as waste: see below under Chemical Storage.
- Discarded equipment, glassware, sharps, etc. are not classified as hazardous chemical waste if contaminating chemicals are removed prior to disposal.

(b) Satellite Accumulation Areas (SAAs)

- SAAs are areas at the “*point of generation*” of hazardous wastes where wastes are collected in containers for disposal. SAAs are defined by trays or tubs (“secondary containers”) labeled as “Hazardous Waste Satellite Accumulation Areas.” Alternatively, special labeled tape (provided by the EMP) can be used to define an SAA.
- A green EMP SAA sign must be posted in the vicinity of the SAA.
- For a given category of waste, no more than one container is permitted per SAA.
- Containers of incompatible wastes cannot be stored within the same secondary container in an SAA.
- Waste containers can remain indefinitely in an SAA until they are full; then they must be dated and removed within 3 days.
- SAAs must be inspected weekly; although a written inspection log is not required.

(c) Main Storage Areas (MSAs)

- Main Storage Areas are managed by the Environmental Management Program. Contact the EMP to create a new MSA or to shut down or modify an existing one.
- When a waste container is full, it should be transferred from the Satellite Accumulation Area to the laboratory’s MSA. Disposal is then arranged online by completing the form at: <http://ehs.mit.edu/site/content/chemical-waste-collection-form>. Hazardous waste pickup can also be requested by calling the MIT Environmental Management Office (2-3477). The EMP will send an employee or contractor to pick up and transport the materials to the special storage area maintained by the EMP. Containers can be stored in the laboratory MSA for no more than 90 days.
- MSAs should generally be flammable chemical storage cabinets labeled with the EMP “Hazardous Waste” sign with NFPA hazard diamond and green and white tape.
- Incompatible wastes must be segregated in the MSA cabinet using secondary containers where necessary.
- If non-waste chemicals must be stored within the same cabinet, then the waste containers must be segregated in a section of the cabinet clearly defined with special tape available from the EMP.
- MSAs are inspected weekly by EMP personnel who maintain inspection logs.

(d) Waste Containers

- Separate containers should be used for different categories of chemical wastes and only

compatible chemicals should be combined.

- Containers must be sealed when not in use to prevent emission of volatile chemicals and to prevent spillage if the container is knocked over. This rule also applies to containers of solid waste.
- Waste containers must be kept within an SAA or MSA at all times.
- Old labels must be removed from containers or defaced.
- An EMP **Red Hazardous Waste Tag** must be attached to a container as soon as it is first used for the storage of waste chemicals. The identity (by name, not formula) of all chemicals present in greater than ca. 1% concentration should be listed. The appropriate hazard boxes should be checked off on the tag. Red tags should be protected from smearing by enclosure in a zip-lock baggie. Red tags should only be dated when the container becomes full. At that point the container can only be stored in the SAA for 3 days.
- Any chemicals spilled on the outside of a container should be immediately cleaned off.

(e) Procedures for Specific Classes of Excess and Waste Chemicals

(1) *Liquid Organic Chemicals*

The local regulations that govern the MIT sewer system expressly prohibit the discharge of organic solvents into the system. No liquid organic chemicals should be disposed of “down the drain,” and this rule applies to all solvents whether or not they are miscible with water. Rotary evaporators should always be equipped with effective cooling condensers to trap all solvent vapors. If a dry ice (-78 °C) cold-finger condenser is not used, then a dedicated pump system should be employed instead of a water aspirator. Excess and waste liquid organic chemicals should be stored in appropriate containers as outlined above and sent to the EMP Waste Chemicals Storage Area (WCSA). *Compatible* mixtures of liquid organic compounds can be stored in one container provided that the Red Tag indicates the relative proportion of each component. *Halogenated compounds (e.g. chloroform) should be segregated in separate containers from other organic compounds.* Note that chlorinated solvents form explosive mixtures with certain other compounds (e.g. with some amines, with acetone in the presence of base, etc.). Ethereal solvents (diethyl ether, THF, dioxane, DME, etc.) should be stored in glass containers and diluted with water. Prolonged storage of ethers should be avoided since they can form explosive peroxides upon standing.

(2) *Aqueous Solutions*

Excess and waste aqueous solutions should be stored in appropriate containers and sent to the EMP waste storage area as outlined above. Aqueous solutions of acids and bases, and aqueous solutions containing hazardous chemicals cannot be disposed of “down the drain” under any circumstances.

(3) *Solid Inorganic and Organic Chemicals*

Excess and waste solid chemicals can often be sent to the Waste Chemical Storage Area (WCSA) in their original containers. Compatible solids can be stored in one container provided that the Red Tag indicates the relative proportion of each component. Certain classes of solid waste chemicals require special handling. **Toxic solid wastes** can be sent to the WCSA in properly labeled, tightly sealed containers. Contact the Environmental Health and Safety Office (452-3477) for advice on the handling and packaging of toxic waste chemicals (information on the properties and toxicity of organic and inorganic chemicals can

also be obtained from the references in the Chemistry Department Library of Laboratory Safety). **Alkali metals** such as sodium and potassium should be stored under mineral oil in tightly sealed containers and sent to the WCSA for disposal. Other **pyrophoric metals and compounds** such as magnesium, lithium aluminum hydride, and sodium hydride should be stored in tightly sealed metal containers and may be sent to the WCSA for disposal. Waste **mercury** should be stored in bottles or jars and sent to the WCSA; broken thermometers that contain mercury should be placed in jars and also sent to the WCSA. Consult Chemical Research Safety Note #4 for procedures for handling mercury.

(4) *Unknown Waste Chemicals*

The MIT EMP will **not accept unknown chemicals** for transport to the WCSA. This is due to the fact that our outside contractors are prohibited from accepting unidentified materials for disposal. It is the responsibility of the research group generating the material to determine the chemical identity of the unknown waste; in some cases this may require paying for the services of an outside analytical laboratory. Once the composition of the waste material is known, it can then be disposed of according to the procedures outlined above.

(5) *Gas Cylinders*

Gas cylinders are **not** sent to the WCSA for disposal. To arrange pickup of excess and empty gas cylinders go to <http://airgas.mit.edu/pickup-request> or contact Airgas at (56-022, x3-4761). Small “lecture-bottle-type” cylinders will also not be accepted for disposal. Contact the EMP (452-3477) for further information on how to dispose of or return small cylinders.

Whenever possible, avoid purchasing chemicals in non-returnable lecture bottles, since the disposal of these cylinders has become extremely expensive. It is recommended that you save the shipping crate, warning labels, valve covers, etc., so that your cylinders can be returned to the vendor in accordance with the Department of Transportation’s regulations and the vendor’s procedures. All researchers are required to have their empty cylinders returned to the vendor before leaving MIT.

The disposal of several other categories of excess and waste materials are governed by special regulations. Materials of this type include (contact indicated office for information on disposal):

Controlled drugs (contact Scott Ide, 324-6132)

Radioactive materials (contact Radiation Protection Program, 452-3477)

Biological wastes (contact Biosafety Program, 452-3477)

Polychlorinated biphenyls (PCBs) (contact EMP, 452-3477)

(13) Procedures for Handling the Accidental Release of Hazardous Substances

Minor hazardous material or waste spills that present no immediate significant threat to personnel safety or health, or to the environment should be cleaned up by the laboratory personnel using the materials or generating the waste. A **minor (“incidental”) hazardous material spill** is generally defined as a spill of material that is not highly toxic, is not spilled in large quantity, does not present a significant fire hazard, can be recovered before it is released to the environment, and is not in a public area such as a common hallway. Such a spill can usually be controlled and cleaned up by one or two personnel. Note that custodians are not permitted to clean up such spills. The Environmental Health and Safety Office will provide technical advice, but is not responsible for spill cleanup.

Major (“non-incident”) hazardous material and waste spills should be reported to the MIT emergency number (x100) to obtain immediate professional assistance and support to control and clean up the spilled material. Major hazardous material or waste spills are generally defined as posing a significant threat to safety, health, or the environment. These spills generally involve a highly toxic material or material spilled in large quantity, may present a significant fire hazard, cannot be recovered before release to the environment, or involve a spill in a public area such as a common hallway. After reporting such a spill, personnel should stand by at a safe distance to guide responders and spill clean up experts to the spill area. Reporting personnel should also keep other personnel from entering into the spill area.

MIT has written plans and relationships with outside contractors to control and clean up major spills of hazardous materials and waste.

Experiments should always be designed so as to minimize the possibility of an accidental release of hazardous substances. Plan your experiments to use the minimal amounts of hazardous compounds practical and always transport such materials properly using break-resistant bottles or secondary containers. As discussed further below, develop a contingency plan to handle spills when working with hazardous substances. In the event that a spill does occur, the following *General Guidelines for Handling Spills* should be followed in the indicated order of priority.

1. Notify other personnel of the accident, and if necessary, evacuate the area.
2. Tend to any injured or contaminated personnel and, if necessary, request help (call the MIT emergency number 100 or activate a fire alarm, or both).
3. In the case of minor spills, take steps to confine and limit the spill if this can be done without risk of injury or contamination.
4. In the case of minor spills, clean up the spill and dispose of contaminated materials properly according to the procedures described in section (10) of Part V-C above.

The following section outlines *specific procedures* for handling the accidental release of hazardous substances.

(a) **Preplanning to Control Spills**

Be familiar with the properties (physical, chemical, and toxicological) of hazardous substances before working with them. Develop a contingency plan to deal with the accidental release of each hazardous substance. Make sure that the necessary safety equipment, protective apparel, and spill control materials are readily available.

Every research group that works with hazardous substances should have a **Group Spill Kit** tailored to deal with the potential hazards of the materials being used in their laboratory. Group EHS Representatives are responsible for maintaining these spill control kits. Spill kits should be located near laboratory exits for ready access. Typical spill control kits might include:

- (i) **Spill control pillows and pads** (commercially available from Lab Safety Supply, American Scientific Products, and other companies). These generally can be used for absorbing solvents, acids, caustic alkalis, but not HF.
- (ii) **Inert absorbents** such as vermiculite, clay, and sand.
- (iii) **Neutralizing agents for acid spills** such as sodium carbonate and sodium bicarbonate.
- (iv) **Neutralizing agents for alkali spills** such as sodium bisulfate and citric acid.
- (v) **Large plastic scoops** and other equipment such as brooms, pails, bags, dust pans, etc., as appropriate.

(b) **Treating Injured and Contaminated Personnel**

If an individual is injured or contaminated with a hazardous substance, then tending to them will generally take priority over the spill control measures outlined below. It is important to obtain medical attention as soon as possible; call 100, the Campus Police 24-hour line in the event of an emergency.

For spills covering small amounts of skin, immediately flush with flowing water for no less than fifteen minutes. If there is no visible burn, wash with warm water and soap, remove any jewelry to facilitate removal of any residual materials. Check the SDS to see if any delayed effects should be expected. It is advisable to seek medical attention for even minor chemical burns. For spills on clothes, don't attempt to wipe the clothes. Quickly remove all contaminated clothing, shoes and jewelry while using the safety shower. Seconds count, and no time should be wasted because of modesty. Be careful not to spread the chemical on the skin, or especially in the eyes. Use caution when removing pullover shirts or sweaters to prevent contamination of the eye; it may be better to cut the garments off. Immediately flood the affected body area with warm water for at least 15 minutes. Resume if pain returns. Do not use creams, lotions or salves. Get medical attention as soon as possible. Contaminated clothes should be discarded or laundered separately from other clothing.

For splashes into the eye, immediately flush the eye with tempered potable water from a gently flowing source for at least 15 minutes. Hold the eyelids away from the eyeball, move the eye up and down and sideways to wash thoroughly behind the eyelids. An eyewash should be used, but if one is not available, injured persons should be placed on their backs and water gently poured into their eyes for at least fifteen minutes. First aid must be followed by prompt treatment by a member of a medical staff or an ophthalmologist especially alerted and acquainted with chemical injuries.

(c) **Notify Personnel in the Area**

Alert other workers in the laboratory of the accident and the nature of the chemicals involved. In the event of the release of a highly toxic gas or volatile material, evacuate the laboratory and post personnel at all entrances to prevent other workers from inadvertently entering the contaminated area. In the case of major "non-incident" spills (see above; spills involving the release of highly toxic substances, occurring in non-laboratory areas, etc.), it may be appropriate to activate a fire alarm to alert personnel to evacuate the building. Call 100 to obtain emergency assistance from the Cambridge Fire Department and MIT EHS Office.

(d) **Clean Up Spills Promptly**

Specific procedures for cleaning up spills will vary depending on the location of the accident (elevator, corridor, chemical storeroom, laboratory hood), the amount and physical properties of the spilled material (volatile liquid, solid, or toxic gas), and the degree and type of toxicity. Outlined below are some general guidelines for handling several common minor ("incidental") spill situations; for more information, see "Tested Methods for the Handling of Small-Scale Spills," M.-A. Armour, D. Ashick, and J. Konrad, *Chemical Health & Safety* 1999, 6, Jan-Feb, 24-27 (copy available in the Library of Lab Safety).

(i) **Materials of low flammability which are not volatile or which have low toxicity.**

This category of hazardous substances includes inorganic acids (sulfuric, nitric) and caustic bases (sodium and potassium hydroxide). For clean-up, wear appropriate protective apparel including gloves, goggles, and (if necessary) shoe-coverings. Neutralize the spilled chemicals

with materials such as sodium bisulfate (for alkalis) and sodium carbonate or bicarbonate (for acids). Absorb the material with inert clay or vermiculite, scoop it up, and dispose of it according to the procedures detailed above in Part V-C, section (10).

- (ii) **Flammable solvents.** Fast action is crucial in the event that a flammable solvent of relatively low toxicity is spilled. This category includes pet ether, hexane, pentane, diethyl ether, dimethoxyethane, and tetrahydrofuran. Immediately alert other workers in the laboratory, extinguish all flames, and turn off any spark-producing equipment. In some cases the power to the lab should be shut off with the circuit-breaker. As quickly as possible, the spilled solvent should be soaked up using spill control pillows or pads. These should be sealed in containers and disposed of properly.
- (iii) **Highly toxic substances.** Do not attempt to clean up a spill of a highly toxic substance by yourself. Notify other personnel of the spill, evacuate the area, and contact the EHS Office (452-3477) to obtain assistance in evaluating the hazards involved. The Cambridge Fire Department and the IHP have special protective equipment to permit safe entry into areas contaminated with highly toxic substances.

(e) Handling Leaking Gas Cylinders

Occasionally, a cylinder or one of its component parts develops a leak. Most such leaks occur at the top of the cylinder in areas such as the valve threads, safety device, valve stem, and valve outlet. If a leak is suspected, do not use a flame for detection; rather, a flammable-gas leak detector or soapy water or other suitable solution should be used. If the leak cannot be remedied by tightening a valve gland or a packing nut, emergency action procedures should be effected and the supplier should be notified. Laboratory workers should never attempt to repair a leak at the valve threads or safety device; rather, they should consult with the supplier for instructions.

The following general procedures can be used for relatively minor leaks where the indicated action can be taken without the exposure of personnel to highly toxic substances. Note that if it is necessary to move a leaking cylinder through populated portions of the building, place a plastic bag, rubber shroud, or similar device over the top and tape it (duct tape preferred) to the cylinder to confine the leaking gas.

- (i) **Flammable, inert, or oxidizing gases** - Move the cylinder to an isolated area (away from combustible material if the gas is flammable or an oxidizing agent) and post signs that describe the hazards and state warnings. If feasible, leaking cylinders should always be moved into laboratory hoods.
- (ii) **Corrosive gases** may increase the size of the leak as they are released and some corrosives are also oxidants or flammable. Move the cylinder to an isolated, well-ventilated area and use suitable means to direct the gas into an appropriate chemical neutralizer. Post signs that describe the hazards and state warnings.
- (iii) **Toxic gases** - Follow the same procedure as for corrosive gases. Move the cylinder to an isolated, well-ventilated area and use suitable means to direct the gas into an appropriate chemical neutralizer. Post signs that describe the hazards and state the warnings.

When the nature of the leaking gas or the size of the leak constitutes a more serious hazard, self-contained breathing apparatus and protective apparel may be required. Evacuate personnel from the affected area (activate the fire alarm to order the evacuation of the building) and call Campus Police (dial 100) to obtain emergency assistance.

(14) Special Precautions for Work with Nanomaterials

Nanomaterials are defined by the ASTM as a material with two or three dimensions between 1 to 100 nm. They can be composed of many different base materials (carbon, silicon, and metals such as gold, cadmium, and selenium). They can also have different shapes: such as nanotubes, nanowires, crystalline structures such as quantum dots, and fullerenes. Nanomaterials often exhibit very different properties from their respective bulk materials: greater strength, conductivity, and fluorescence, among other properties.

The toxicity of most nanomaterials is currently unknown. Preliminary toxicity testing has indicated that some nanoparticles may be more toxic than the corresponding micron sized particle because of their greater surface area and reactivity. Nano-sized titanium dioxide produces 40 fold more lung inflammation than micron-sized particles. In preliminary tests, carbon nanotubes have produced lung inflammation and fibrosis similar to crystalline quartz and asbestos. Nanoparticles are similar in size to viruses and are easily taken up by the body's cells, translocate around the body, and can possibly pass into the brain and through the skin.

The MIT EHS Office considers nanoparticles that have the potential for release into the air to be handled as particularly hazardous substance because their toxicity is, for the most part, unknown and early studies have been suggestive of toxic effects. In the future, many types of nanoparticles may turn out to be of limited toxicity but precaution should be used until more is known. Work with nanoparticles that may release particles should be conducted in enclosures, glove boxes, fume hoods, and other vented enclosures. All work should be done with gloves, at a minimum disposable nitrile gloves. More information on additional precautions and a review of the toxicity of some types of nanomaterials are on the EHS web site at:

<http://ehs.mit.edu/site/content/working-safely-nanomaterials>

This article also lists good reference sources for researchers to consult to keep up with toxicity information on their materials as it develops. Currently, nanoparticles and solutions containing them are being disposed of as hazardous waste. Please call the EHS Office at 452-3477 for exposure evaluation of experimental setups

D. General Procedures for Working with Flammable, Pyrophoric and Explosive Substances

Flammable substances are among the most common of the hazardous materials found in the laboratories of the Chemistry Department. Flammable substances are materials that readily catch fire and burn in air. A flammable liquid does not itself burn; it is the vapors from the liquid that burn. The rate at which different liquids produce flammable vapors depends on their vapor pressure, which increases with temperature. The degree of fire hazard depends also on the ability to form combustible or explosive mixtures with air, the ease of ignition of these mixtures, and the relative densities of the liquid with respect to water and of the gas with respect to air.

An open beaker of diethyl ether set on the laboratory bench next to a Bunsen burner will ignite, whereas a similar beaker of diethyl phthalate will not. The difference in behavior is due to the fact that the ether has a much lower flash point. The flash point is the lowest temperature, as determined by standard tests, at which a liquid gives off vapor in sufficient concentration to form an ignitable mixture with air near the surface of the liquid within the test vessel. As indicated in the following table, many common laboratory solvents and chemicals have flash points that are lower than room temperature and are potentially very dangerous.

	Flash Point (°C)		Flash Point (°C)
Acetone	-17.8	Ethanol	12.8
Benzene	-11.1	Hexane	-21.7
Carbon disulfide	-30.0	Methanol	11.1
Cyclohexane	-20.0	Pentane	-40.0
Diethyl ether	-45.0	Toluene	4.4

Handling Flammable Substances

The following basic precautions should be followed in handling flammable substances.

1. Flammable substances should be handled only in areas free of ignition sources. Besides open flames, ignition sources include electrical equipment (especially motors), static electricity, and for some materials (e.g. carbon disulfide), even hot surfaces. Heat guns should never be used in areas where the vapor of flammable liquids are present.
2. Never heat a flammable substance with an open flame.
3. When transferring flammable liquids in metal equipment, static-generated sparks should be avoided by bonding and the use of ground straps.
4. Ventilation is one of the most effective ways to prevent the formation of flammable mixtures. A laboratory hood should be used whenever appreciable quantities of flammable substances are transferred from one container to another, allowed to stand or heated in open containers, or handled in any other way. Be sure that the hood is free of all ignition sources including, in particular, variacs.
5. Safety goggles, gloves, and a flame resistant lab coat should be worn when working with flammable substances. Flame resistant cotton based coats treated with a flame retardant are acceptable, but Nomex lab coats offer increased protection. Exceptions to the requirement for flame resistant lab coats can be approved for certain well defined research such as work with very small quantities of flammable solvents. Requests for such exceptions should be submitted by the PI for the research group to EHS Coordinator, Scott Ide for approval by the EHS Committee.

Handling Pyrophoric Substances

Pyrophoric substances are materials that can spontaneously ignite in air. Special procedures are required for the safe use of pyrophorics and researchers should not work with these materials unless they are certain they have enough information and training to use them without significant risk. An excellent document which may serve as a starting point for learning the proper procedures for handling pyrophoric compounds can be found at the following url http://www.chemistry.ucla.edu/sites/default/files/safety/sop/SOP_Pyrophoric_Liquid_Reagents.pdf. When working with pyrophorics, safety goggles, gloves, and a lab coat made of fire retardant Nomex material should be worn.

Handling Explosive Substances

Explosive substances are materials that decompose under conditions of mechanical shock, elevated temperature, or chemical action, with the release of large volumes of gases and heat. Special precautions are required for the safe use of explosive materials. *It is the responsibility of the researcher to evaluate the explosive hazards involved in their work and to consult with their supervisor to develop detailed standard operating procedures for any work involving explosive substances.* Work with explosive materials will generally require the use of special protective apparel (face shields, gloves, lab coats) and protective devices such as explosion shields and barriers.

Organic peroxides are among the most hazardous substances handled in Chemistry Department laboratories. As a class, they are low-power explosives, hazardous because of their sensitivity to shock, sparks, and even friction (as in a cap being twisted open). Many peroxides that are routinely handled in laboratories are far more sensitive to shock than most primary explosives such as TNT. All organic peroxides are highly flammable, and most are sensitive to heat, friction, impact, light, as well as strong oxidizing and reducing agents.

Some peroxides in use in the Department are commercial compounds such as *m*-chloroperoxybenzoic acid, benzoyl peroxide, hydrogen peroxide, and *t*-butyl hydroperoxide. However, many common solvents and reagents are known to form peroxides on exposure to air, and these chemicals often become contaminated with sufficient peroxides to pose a serious hazard. Classes of compounds that form peroxides by autoxidation include:

- (a) **Aldehydes** including acetaldehyde and benzaldehyde,
- (b) **Ethers** with primary and/or secondary alkyl groups, including acyclic and cyclic ethers, acetals, and ketals. Examples include diethyl ether, diisopropyl ether (especially dangerous!), dioxane, DME, THF, ethyl vinyl ether and alcohols protected as THP ethers. Isopropyl alcohol also frequently forms peroxides upon storage.
- (c) **Hydrocarbons with allylic, benzylic, or propargylic hydrogens.** Examples of this class of peroxide-formers include cyclohexene, cyclooctene, methyl acetylene, isopropylbenzene (cumene), and tetralin (tetrahydronaphthalene).
- (d) **Conjugated dienes, enynes, and diynes**, among which divinylacetylene is particularly hazardous.
- (e) **Saturated hydrocarbons with exposed tertiary hydrogens;** common peroxide-formers include decalin (decahydronaphthalene) and 2,5-dimethylhexane.

Compounds belonging to the classes listed above cannot form peroxides without exposure to oxygen (or other oxidizers). Consequently, when storing these materials always flush the container with an inert gas such as nitrogen or argon before sealing. If the compound is not volatile, it may be advisable to degas the sample by vacuum or bubbling techniques. In some cases it may be appropriate

to add an oxidation inhibitor such as hydroquinone or BHT (2,6-di-*t*-butyl-4-methylphenol) to the sample. Containers should be tightly sealed and dated upon receipt and when first opened. Recommended safe storage limits vary depending on the identity of the material and exposure to light and air, but can be as low as 3 months. Do not attempt to open bottles of liquid ethers (e.g. diisopropyl ether) containing crystallized material; contact the EMP (452-3477) for assistance in disposal.

Before distilling any known or suspected peroxide-former, check it carefully for the presence of peroxides. Containers should also be checked periodically after extended storage. Either of the following tests will detect most (but not all) peroxy compounds including all hydroperoxides:

Add 1-3 mL of the liquid to be tested to an equal volume of acetic acid, add a few drops of 5% aqueous KI solution, and shake. The appearance of a yellow to brown color indicates the presence of peroxides.

Add 0.5 mL of the liquid to be tested to a mixture of 1 mL of 10% aqueous KI solution and 0.5 mL of dilute HCl to which has been added a few drops of starch solution just prior to the test. The appearance of a blue or blue-black color within a minute indicates the presence of peroxides.

Low concentrations of peroxides can generally be removed by filtering the contaminated material through a column of chromatography-grade basic alumina. Several methods are available for the “deperoxidation” of ether solvents; for a discussion, see Burfield, D. R. J. *Org. Chem.* 1982, 47, 3821. To destroy small quantities (25 g or less) of peroxides, dilute with water (to a concentration of 2% or less) and then transfer to an aqueous solution of an appropriate reducing agent (such as ferrous sulfate or sodium bisulfite) in a polyethylene container.

More information on this topic can be found in the article “Review of Safety Guidelines for Peroxidizable Organic Chemicals,” R. J. Kelly, *Chemical Health and Safety* 1996, 3, 28-36, Sept-Oct, 28-36 (copy available in the Library of Lab Safety). The MIT EHS website has information regarding expiration dates, testing and disposal of peroxide forming chemicals which can be found at the following link: <https://ehs.mit.edu/site/content/peroxide-forming-chemicals-0>. For assistance in disposing of larger quantities of peroxides or other explosive materials, contact the EMP at 253-4736.

Activation of Building Alarm System

Any fire which is not immediately extinguished requires immediate evacuation and activation of the nearest fire alarm pull station. After evacuating to a safe location, call Campus Police (x 100). Stay on the phone until the dispatcher instructs you to hang up or it becomes unsafe to remain on the phone in your current location. Be prepared to meet and advise the Fire Department and Emergency Response Team with regard to the hazards present in your laboratory.

When the Fire Alarm sounds, all personnel are required to leave the building.

Control or Fighting of Fires

MIT personnel are not required or expected to fight fires. However, there may be certain instances when small fires can be extinguished without risk of personal injury as outlined below.

1. **Fires in small vessels** can usually be suffocated by loosely covering the vessel. Never pick up a flask or container of burning material. Small amounts of ordinary combustible material such as paper towels or a cotton swab can also usually be extinguished by covering the burning material with a glass or metal cover large enough to suffocate the burning material. Fires of this type should be reported promptly to your Laboratory Supervisor in order to help prevent future incidents in similar laboratory operations.

2. A **small fire which has just started** can sometimes be extinguished with a laboratory fire extinguisher. *Extinguishing such fires should only be attempted if there is no risk of personal injury by individuals who have attended a fire extinguisher familiarization session at MIT, and only if you are confident that you can do so successfully and quickly, and from a position in which you are always between the fire and an exit from the laboratory.* Do not underestimate fires, and remember that toxic gases and smoke may present additional hazards.
3. **Small fires involving reactive metals and organometallic compounds** (such as magnesium, sodium, potassium, metal hydrides, etc.) can be extinguished *if there is no risk of personal injury* with Met-L-X or Met-L-Kyl (see Part IV-E), or by covering with dry sand. Extinguishing such fires should only be attempted by properly trained personnel.

Reporting of Fires

Small fires which are immediately extinguished should be reported to your Supervisor.

More serious fires which are immediately extinguished but require the use of a fire extinguisher, result in damage to laboratory fixtures, or that result in injury to lab personnel must be reported in writing to the Department EHS Coordinator, and by phone to the EHS Office (x 2-EHSS). Note that is particularly important to immediately report fires that occur in fume hoods to the EHS Office or to Campus Police (x 100) in the case of fires occurring at night, on holidays, or on weekends. This is essential because sparks and embers can travel through the hood system and ductwork igniting other materials at points far away from the hood.

Guidelines to Prevent and Minimize Injury and Damage From Fires

1. **Be prepared!** Know the location of at least two exits from your work area. Personnel who have received proper training in the use of fire extinguishers should know where all of the fire extinguishers are located in their laboratory, what types of fires they can be used for, and how to correctly operate them. Know where the nearest fire alarm is located. Know the location of safety showers and fire blankets.
2. **Personal injuries involving fires.** Minor clothing fires can sometimes be extinguished by immediately dropping to the floor and rolling. If a person's clothing catches fire, they should be doused with water from the safety shower. Fire blankets should only be used as a last-resort measure to extinguish fires since they tend to hold in heat and to increase the severity of burns. Quickly remove contaminated clothing, douse the person with water, and place clean, wet, cold cloth on burned areas. Wrap the injured person in a blanket to avoid shock and get medical attention promptly.

Specific Hazards That May Lead to Fires or Explosions

The combination of certain compounds or classes of compounds can result in a violent chemical reaction leading to an explosion or fire. Other compounds pose explosion or fire hazards when exposed to heat, shock, or other conditions. Listed below are some of the specific compounds and combinations of compounds that may pose explosion or fire hazards and may be encountered in Chemistry Department laboratories. This list is not intended to be complete, and researchers should always be familiar with the flammability and other properties of the chemicals involved in their research.

1. **Acetylenic compounds** are explosive in mixtures of 2.5-80% with air. At pressures of 2 or more atmospheres, acetylene subjected to an electrical discharge or high temperature

decomposes with explosive violence. Dry acetylides can detonate on receiving the slightest shock. Many heavy metal acetylides are sensitive explosives.

- Aluminum chloride** should be considered a potentially dangerous material. If moisture is present, there may be sufficient decomposition (generating HCl) to build up considerable pressure. If a bottle is to be opened after long standing, it should be completely enclosed in a heavy towel.
- Ammonia** reacts with iodine to give nitrogen triiodide, which is explosive, and with hypochlorites to give chlorine. Mixtures of ammonia and organic halides sometimes react violently when heated under pressure.
- Azides** such as sodium azide can displace halide from chlorinated hydrocarbons such as dichloromethane to form highly explosive organic polyazides; this substitution reaction is facilitated by the presence of solvents such as DMSO.
- Dry **benzoyl peroxide** is easily ignited and sensitive to shock and may decompose spontaneously at temperatures above 50°C. It is reported to be desensitized by addition of 20% water.
- Carbon disulfide** is both very toxic and very flammable; mixed with air, its vapors can be ignited by a steam bath or pipe, a hot plate, or by a glowing light bulb.
- Chlorine** may react violently with hydrogen or with hydrocarbons when exposed to sunlight.
- Diazomethane** and related compounds should be treated with extreme caution. They are very toxic (potent carcinogens), and the pure gases and liquids explode readily. Solutions in ether are safer with regard to shock sensitivity.
- Dimethyl sulfoxide** decomposes violently on contact with a wide variety of active halogen compounds. Explosions from contact with active metal hydrides have been reported.
- Diethyl, diisopropyl, and other ethers** (particularly the branched-chain type) sometimes explode during heating or refluxing because of the presence of peroxides. Ferrous salts or sodium bisulfite can be used to decompose these peroxides, and passage over basic active alumina will remove most of the peroxidic material. In general, however, old samples of ethers should be carefully and properly disposed of.
- Ethylene oxide** has been known to explode when heated in a closed vessel. Experiments using ethylene oxide under pressure should be carried out behind suitable barricades.
- Halogenated compounds** such as chloroform, carbon tetrachloride, and other halogenated solvents should not be dried with sodium, potassium, or other active metals; violent explosions usually occur upon treatment of these solvents with active metals.
- Hydrogen peroxide** stronger than 3% can be dangerous: in contact with the skin, it may cause severe burns. Thirty percent hydrogen peroxide can decompose violently if contaminated with iron, copper, chromium, or other metals or their salts.
- Liquid-nitrogen** cooled traps open to the atmosphere rapidly condense liquid air. When the coolant is later removed, an explosive pressure buildup can then occur, usually with enough force to shatter glass equipment. Hence, only sealed or evacuated equipment should be cooled with liquid nitrogen.
- Lithium aluminum hydride** should not be used to dry ethyl ether or tetrahydrofuran; fires from this are very common. The products of the reaction of LAH with carbon dioxide have been reported to be explosive. Carbon dioxide or bicarbonate extinguishers should not be used against lithium aluminum hydride fires, which should be smothered with sand or some other inert substance.

16. **Oxygen tanks:** Serious explosions have resulted from contact between oil and high-pressure oxygen. Oil should not be used on connections to an oxygen cylinder.
17. **Ozone** is a highly reactive and toxic gas. It is formed by the action of ultraviolet light on oxygen (air) and, therefore, certain ultraviolet sources may require venting to the exhaust hood. Liquid and solid ozone are explosive substances.
18. **Palladium or platinum on carbon, platinum oxide, Raney nickel, and other catalysts** should be filtered from catalytic hydrogenation reaction mixtures carefully. The recovered catalyst is usually saturated with hydrogen and highly reactive and thus will enflame spontaneously on exposure to air. When filtering hydrogenation reaction mixtures (particularly large-scale reactions), the filter cake should not be allowed to become dry. The funnel containing the still-moist catalyst filter cake should be put into a water bath immediately after completion of the filtration. Note that another hazard in working with such catalysts is the danger of explosion if additional catalyst is added to a flask in which hydrogen is present.
19. **Parr bombs** used for hydrogenations have been known to explode. They should be handled with care behind shields, and the operator should wear goggles.
20. **Perchlorates:** The use of perchlorates should be avoided whenever possible. Perchlorates should not be used as drying agents if there is a possibility of contact with organic compounds, or if they will be in proximity to a dehydrating acid strong enough to concentrate the perchloric acid to more than 70% strength (e.g., in a drying train that has a bubble counter containing sulfuric acid). Safer drying agents should be used. Seventy percent perchloric acid can be boiled safely at approximately 200 °C, but contact of the boiling undiluted acid or the hot vapor with organic matter, or even easily oxidized inorganic matter (such as compounds of trivalent antimony), will lead to serious explosions. Oxidizable substances must never be allowed to contact perchloric acid. Beaker tongs, rather than rubber gloves, should be used when handling fuming perchloric acid. Perchloric acid evaporations should be carried out in a hood that has a good draft and a built-in water spray for the ductwork behind the baffle. Frequent (weekly) washing out of the hood and ventilator ducts with water is necessary to avoid danger of spontaneous combustion or explosion if this acid is in common use.
21. **Permanganates** are explosive when treated with sulfuric acid. When both compounds are used in an absorption train, an empty trap should be placed between them.
22. **Peroxides (inorganic)** when mixed with combustible materials, barium, sodium, and potassium peroxides form explosives that ignite easily.
23. **Phosphorus** (red and white) forms explosive mixtures with oxidizing agents. White P should be stored under water because it is spontaneously flammable in air. The reaction of P with aqueous hydroxides produces highly toxic phosphine, which may ignite spontaneously in air or explode.
24. **Phosphorus trichloride** reacts with water to form phosphorous acid which decomposes on heating to form phosphine, which may ignite spontaneously or explode. Care should be taken in opening containers of phosphorous trichloride, and samples that have been exposed to moisture should not be heated without adequate shielding to protect the operator.
25. **Potassium** is in general more reactive than sodium; it ignites quickly on exposure to humid air and, therefore, should be handled under the surface of a hydrocarbon solvent such as mineral oil or toluene. Oxidized coatings should be carefully scraped away before cutting potassium metal as explosions can otherwise occur.

26. **Residues from vacuum distillations** have been known to explode when the still apparatus was vented to the air before the distillation pot residue was cool. Such explosions can be avoided by venting the still pot with nitrogen, by cooling it before venting, and by restoring the pressure slowly.
27. **Sodium** should be stored in a closed container under kerosene, toluene, or mineral oil. Scraps of Na or K should be destroyed by reaction with *n*-butyl alcohol. Contact with water should be avoided because Na reacts violently with water to form hydrogen with evolution of sufficient heat to cause ignition. Carbon dioxide, bicarbonate, and carbon tetrachloride fire extinguishers should *not* be used on alkali metal fires.

When transporting, storing, using, or disposing of any substance, utmost care must be exercised to ensure that the substance cannot accidentally come in contact with another material with which it is incompatible. Such contact could result in a serious explosion or the formation of substances that are highly toxic or flammable or both. The following Table is a guide to avoiding accidents involving **incompatible substances**.

Examples of Incompatible Chemicals

Chemical	Is Incompatible With
Acetic acid	Chromic acid, nitric acid, perchloric acid, peroxides, permanganates
Acetylene	Chlorine, bromine, copper, fluorine, silver, mercury
Acetone	Concentrated nitric acid and sulfuric acid mixtures
Alkali and alkaline earth metals) (such as powdered aluminum or magnesium, calcium, lithium, sodium, potassium	Water, carbon tetrachloride or other chlorinated hydrocarbons, carbon dioxide, halogens
Ammonia (anhydrous)	Mercury (in manometers, for example), chlorine, calcium hypochlorite, iodine, bromine, hydrofluoric acid (anhydrous)
Ammonium nitrate	Acids, powdered metals, flammable liquids, chlorates, nitrites, sulfur, finely divided organic or combustible materials
Aniline	Nitric acid, hydrogen peroxide
Arsenical materials	Any reducing agent
Azides	Acids
Bromine	See Chlorine
Calcium oxide	Water
Carbon (activated)	Calcium hypochlorite, all oxidizing agents
Carbon tetrachloride	Sodium
Chlorates	Ammonium salts, acids, powdered metals, sulfur, finely divided organic or combustible materials
Chromic acid and chromium trioxide	Acetic acid, naphthalene, camphor, glycerol, alcohol, flammable liquids in general

Chemical	Is Incompatible With
Chlorine	Ammonia, acetylene, butadiene, butane, methane, propane (or other petroleum gases), hydrogen, sodium carbide, benzene, finely divided metals, turpentine
Chlorine dioxide	Ammonia, methane, phosphine, hydrogen sulfide
Copper	Acetylene, hydrogen peroxide
Cumene hydroperoxide	Acids (organic or inorganic)
Cyanides	Acids
Decaborane	Carbon tetrachloride and some other halogenated hydrocarbons
Flammable liquids	Ammonium nitrate, chromic acid, hydrogen peroxide, nitric acid, sodium peroxide, halogens
Fluorine	Everything
Hydrocarbons (such as butane, propane, benzene)	Fluorine, chlorine, bromine, chromic acid, sodium peroxide, Hydrocyanic acid, Nitric acid, alkali
Hydrofluoric acid (anhydrous)	Ammonia (aqueous or anhydrous)
Hydrogen peroxide	Copper, chromium, iron, most metals or their salts, alcohols, acetone, organic materials, aniline, nitromethane, combustible materials
Hydrogen sulfide	Fuming nitric acid, oxidizing gases
Hypochlorites	Acids, activated carbon
Iodine	Acetylene, ammonia (aqueous or anhydrous), hydrogen
Mercury	Acetylene, fulminic acid, ammonia
Nitrates	Sulfuric acid
Nitric acid (concentrated)	Acetic acid, aniline, chromic acid, hydrocyanic acid, hydrogen sulfide, flammable liquids, flammable gases, copper, brass, any heavy metals
Nitrites	Acids
Nitroparaffins	Inorganic bases, amines
Oxalic acid	Silver, mercury
Oxygen	Oils, grease, hydrogen, flammable liquids, solids, or gases
Perchloric acid wood, grease, oils	Acetic anhydride, bismuth and its alloys, alcohol, paper,
Peroxides, organic	Acids (organic or mineral), avoid friction, store cold
Phosphorous (white)	Air, oxygen, alkalis, reducing agents
Potassium	Carbon tetrachloride, carbon dioxide, water
Potassium chlorate	Sulfuric and other acids
Potassium perchlorate (see also chlorates)	Sulfuric and other acids

Chemical	Is Incompatible With
Potassium permanganate	Glycerol, ethylene glycol, benzaldehyde, sulfuric acid
Selenides	Reducing agents
Silver	Acetylene, oxalic acid, tartaric acid, ammonium compounds, fulminic acid
Sodium	Carbon tetrachloride, carbon dioxide, water
Sodium nitrite	Ammonium nitrate and other ammonium salts
Sodium peroxide	Ethyl or methyl alcohol, glacial acetic acid, acetic anhydride, benzaldehyde, carbon disulfide, glycerine, ethylene glycol, ethyl acetate, methyl acetate, furfural
Sulfides	Acids
Sulfuric acid	Potassium chlorate, potassium perchlorate, potassium permanganate, (similar compounds of light metals such as sodium, lithium)
Tellurides	Reducing agents

Part VI. Procedures for Working with Particularly Hazardous Substances

A. Identification and Classification of Particularly Hazardous Substances

As discussed in the previous section (Part V) of this Chemical Hygiene Plan, hazardous chemicals are chemicals for which there is scientific evidence that adverse acute or chronic health effects may occur in exposed workers. An agent is an **acute toxin** if its toxic effects are manifested after a single or short-duration exposure. **Chronically toxic agents** show their effects after repeated or long-duration exposure and the effects usually become evident only after a long latency period. Many of the substances in frequent use in the Chemistry Department are classified as *hazardous substances*, and the procedures for working with these chemicals are detailed in Part V. There are some substances, however, that pose such significant threats to human health that they are classified as “**particularly hazardous substances**” (PHS’s). The OSHA Laboratory Standard requires that special provisions be established to prevent the harmful exposure of researchers to PHS’s. General procedures for working with such materials are presented in detail in Parts VI-C and VI-D below.

Chemicals are classified as *particularly hazardous substances* if they belong to one or more of the following three categories. Compounds so classified generally must then be handled using the procedures outlined in Part VI-C below. Note, however, that in some circumstances (e.g. when very small quantities of material are being used) it may not be necessary to employ all of the special precautions described in Part VI-C. It is the responsibility of the laboratory supervisor to determine whether a compound is to be treated as a “particularly hazardous substance” in the context of its specific use in his or her laboratory.

1. Select Carcinogens

Certain potent carcinogens are classified as “select carcinogens” and treated as PHS’s. A select carcinogen is defined in the OSHA Lab Standard as a substance that meets one of the following criteria:

- (a) It is regulated by OSHA as a carcinogen,
- (b) It is listed as “known to be a carcinogen” in the latest *Annual Report on Carcinogens* published by the National Toxicology Program (NTP),
- (c) It is listed under Group 1 (“carcinogenic to humans”) by the *International Agency for Research on Cancer* (IARC), or
- (d) It is listed under IARC Group 2A or 2B, (“probably carcinogenic to humans”) or under the category “reasonably anticipated to be a carcinogen” by the NTP, *and* causes statistically significant tumor incidence in experimental animals in accordance with any of the following criteria: (i) after inhalation exposure of 6–7 hours per day, 5 days per week, for a significant portion of a lifetime to dosages of less than 10 mg/m³; (ii) after repeated skin application of less than 300 mg/kg of body weight per week; or (iii) after oral dosages of less than 50 mg/kg of body weight per day.

The following Table lists the substances meeting criteria (a), (b), or (c). For information on compounds meeting criteria (d), see copies of the IARC Group 2A and 2B lists and the NTP lists which are available in the Department Library of Lab Safety.

Partial List of Select Carcinogens

2-acetylaminofluorene	dimethyl sulfate
acrylamide	ethylene dibromide
acrylonitrile	ethylene oxide
4-aminobiphenyl	ethylenimine
arsenic and certain arsenic compounds	formaldehyde
asbestos	hexamethylphosphoramide
azathioprine	hydrazine
benzene	melphalan
benzidine	4,4'-methylene-bis(2-chloroaniline)
bis(chloromethyl) ether	mustard gas
1,4-butanediol dimethylsulfonate (myleran)	N,N'-bis(2-chloroethyl)-2-naphthylamine (chlornaphazine)
chlorambucil	α -naphthylamine
chloromethyl methyl ether	β -naphthylamine
chromium and certain chromium compounds	nickel carbonyl
coal-tar pitches	4-nitrobiphenyl
coal tars	N-nitrosodimethylamine
conjugated estrogens	β -propiolactone
cyclophosphamide	thorium dioxide
1,2-dibromo-3-chloropropane	treosulphan
3,3'-dichlorobenzidine (and its salts)	vinyl chloride
diethylstilbestrol	
dimethylaminoazobenzene	

Note: the above list is not intended to be complete, and it is the responsibility of the researcher (in consultation with their laboratory supervisor) to evaluate each compound involved in their work and to determine whether it should be handled as a select carcinogen.

2. Reproductive and Developmental Toxins

Reproductive toxins act during pregnancy and cause adverse effects on the fetus; these effects include embryoletality (death of the fertilized egg, embryo or fetus), malformations (teratogenic effects), and postnatal functional defects. Examples of embryotoxins include thalidomide and certain antibiotics such as tetracycline. Women of childbearing potential should note that embryotoxins have the greatest impact during the first trimester of pregnancy. *Because a woman often does not know that she is pregnant during this period of high susceptibility, special caution is advised when working with all chemicals, especially those rapidly absorbed through the skin (e.g., formamide).* Pregnant women and women intending to become pregnant should consult with their personal physician, their laboratory supervisor and the Industrial Hygiene Program with regard to the type of work they may safely perform and the special precautions they should take. The contact for this type of work is Robert Edwards (3-9391). All consultations are kept in strict confidence. As minimal precautions, the general procedures outlined in Part VI-C below should then be followed for work with such compounds.

Information on reproductive toxins can be obtained from Safety Data Sheets, by contacting the Industrial Hygiene Program (253-2596), and by consulting the *Catalog of Teratogenic Agents*, Sixth Edition; Shepard, T. H.; Johns Hopkins University Press, Baltimore, 1989. Also see Beyler, R. E. and Meyers, V. K. *J. Chem. Ed.* 1982, 59, 759-763 for a discussion of "What Every Chemist Should Know About Teratogens." The following Table lists some common materials that are suspected to be reproductive toxins; in some laboratories it will be appropriate to handle these compounds as particularly hazardous substances.

Partial List of Reproductive Toxins

arsenic and certain arsenic compounds	lead compounds
benzene	mercury compounds
cadmium and certain cadmium compounds	toluene
carbon disulfide	vinyl chloride
ethylene glycol monomethyl and ethyl ethers	xylene
ethylene oxide	

Note: *The above list is not intended to be complete, and it is the responsibility of the researcher (in consultation with their laboratory supervisor) to evaluate each compound involved in their work and to determine whether it should be handled as a reproductive toxin.*

3. Compounds with a High Degree of Acute Toxicity

Compounds that have a high degree of acute toxicity comprise a third category of particularly hazardous substances as defined by the OSHA Lab Standard. Acutely toxic agents include certain corrosive compounds, irritants, sensitizers (allergens), hepatotoxins, nephrotoxins, neurotoxins, agents that act on the hematopoietic systems, and agents which damage the lungs, skins, eyes, or mucous membranes (see Part V-A for definitions of these classes of hazardous substances). Substances which have a high degree of acute toxicity are interpreted by OSHA as being substances which "may be fatal or cause damage to target organs as the result of a single exposure or exposures of short duration." "Toxic" and "highly toxic" agents are defined by OSHA regulations (29 CFR 1910.1200 Appendix A) as substances with median lethal dose (LD₅₀) values in the following ranges:

	Toxic	Highly Toxic
Oral LD ₅₀ (albino rats)	50-500 mg/kg	<50 mg/kg
Skin Contact LD ₅₀ (albino rabbits)	200-1000 mg/kg	<200 mg/kg
Inhalation LC ₅₀ (albino rats)	200-2000 ppm/air	<200 ppm/air

The following Table lists some of the compounds that may be in current use in Chemistry Department laboratories and which have a high degree of acute toxicity:

Partial List of Compounds with a High Degree of Acute Toxicity

acrolein	nickel carbonyl
arsine	nitrogen dioxide
chlorine	osmium tetroxide
diazomethane	ozone
diborane (gas)	phosgene
hydrogen cyanide	sodium azide
hydrogen fluoride	sodium cyanide (and other cyanide salts)
methyl fluorosulfonate	

Note: the above list is not intended to be complete, and it is the responsibility of the researcher (in consultation with their laboratory supervisor) to evaluate each compound involved in their work and to determine whether it is a substance with a high degree of acute toxicity.

Compounds classified as having a high degree of acute toxicity must generally be handled using the procedures outlined in Part VI-C below. Note, however, that in some circumstances (e.g. when very small quantities of material are being used) it may not be necessary to employ all of the special precautions described in Part VI-C. It is the responsibility of the laboratory supervisor to determine whether a compound with a high degree of acute toxicity is to be treated as a “particularly hazardous substance” in the context of its specific use in his or her laboratory. Finally, several of the compounds listed above require **prior approval** from the Department EHS Committee before work with them can be carried out. See Part VII for a discussion of prior approval requirements.

In evaluating the hazards associated with work with toxic substances, it is important to note that a number of factors influence the response of individuals to exposure to toxic compound. For example, people are rarely exposed to a single biologically active substance. With this point in mind, it is noteworthy that one toxin can influence the effect of a second. Several classic examples are the dramatically enhanced lung carcinogenicity of combined exposure to asbestos and tobacco smoke, and the potentiating activity of phorbol esters on skin carcinogenesis initiated by polycyclic hydrocarbons. There are insufficient data at present to identify which substances potentiate (or possibly even antagonize) the effects of others, but it is important for laboratory workers to be cognizant that such interactions can occur. This point underscores the importance of maintaining good laboratory practices at all times, and with all chemicals.

As a final point, it is also noteworthy that the response of an organism to a toxin typically increases with the dose given, but the relationship is not always a linear one. As one example, some carcinogenic alkylating agents show a biphasic dose-mutation curve resembling a hockey stick pointed upward from left to right. It is now well established that the resistance of many organisms to mutagenesis by low doses of simple alkylating agents is due in large measure to a genoprotective system; once that system saturates, at the breakpoint in the curve, the organism becomes much more sensitive to the toxin. This example illustrates two points. First, we have systems that protect against low doses of many toxins (not all, but many). But, as a second, cautionary note, it is pointed out that between individuals there are differences in the levels of genoprotection and other toxin defense systems. These differences are in part genetically determined but also are determined in part by the aggregate exposure of the individual to all chemicals within and outside of the laboratory. Accordingly, it is difficult to estimate exactly how sensitive a given person will be on a given day to a given substance. This point urges once again that a cautious approach be taken in handling all chemicals in the workplace.

B. Designated Areas

A key requirement of the OSHA Laboratory Standard is that work with particularly hazardous substances must generally be carried out in designated areas. A designated area is defined as a laboratory, an area of a laboratory, or a device such as a laboratory hood which is posted with warning signs that ensure that all employees working in the area are informed of the hazardous substances in use there.

It is the responsibility of laboratory supervisors to define the designated areas in their laboratories and to post these areas with conspicuous signs reading “DESIGNATED AREA FOR USE OF PARTICULARLY HAZARDOUS SUBSTANCES—AUTHORIZED PERSONNEL ONLY.” Printed signs can be obtained from Scott Ide EHS Coordinator (324-6132). In some cases it may be appropriate to post additional signs describing unusual hazards present and/or identifying the specific hazardous substances in use.

Laboratory hoods serve as designated areas for most of the research groups in the Chemistry Department. Laboratory supervisors are required to notify the Department Chemical Hygiene Officer of the specific location of any designated areas established in their research groups *which are not laboratory hoods*.

C. General Procedures for Working with Substances of Moderate to High Chronic Toxicity or High Acute Toxicity

The following general procedures should be followed in work with substances with **high acute toxicity** - i.e. substances that can be fatal or cause serious damage to target organs as the result of a single exposure of short duration. These procedures should also be employed in laboratory operations using those **carcinogens** and **reproductive toxins** for which infrequent, small quantities do not constitute a significant hazard, but which can be dangerous to workers exposed to high concentrations or repeated small doses. A substance that is not known to cause cancer in humans, but which has shown statistically significant, but low, carcinogenic potency in animals, generally should also be handled according to the procedures outlined in this section. Work with more potent carcinogens and reproductive toxins requires the additional precautions described in Part VI-D below. Keep in mind that all of the general rules for work with toxic substances discussed in Part V-C of this Chemical Hygiene Plan also apply to work with “particularly hazardous substances.”

(1) Information.

Before beginning a laboratory operation, each researcher should consult the appropriate literature (see Part III) for information about the toxic properties of the substances that will be used. The precautions and procedures described below should be followed if any of the substances to be used in significant quantities is known to have high acute or moderate chronic toxicity. If any of the substances being used is known to be highly toxic, it is desirable that there be at least two people present in the area at all times. These procedures should also be followed if the toxicological properties of any of the substances being used or prepared are unknown. If any of the substances to be used or prepared are known to have high chronic toxicity (e.g., compounds of certain heavy metals and strong carcinogens), then the precautions and procedures described below should be supplemented with the additional precautions outlined in Part VI-D.

(2) Zero skin contact.

Contact with the skin is a frequent mode of chemical injury. Many toxic substances are absorbed through the skin with sufficient rapidity to produce systemic poisoning. *Avoid all skin contact with*

particularly hazardous substances by using suitable protective apparel including the appropriate type of gloves or gauntlets (long gloves) and a suitable laboratory coat or apron which covers all exposed skin. See Part IV-B for a further discussion of protective apparel. Always wash your hands and arms with soap and water immediately after working with these materials. In the event of accidental skin contact, the affected areas should be flushed with water and medical attention should be obtained as soon as possible.

(3) Use laboratory hoods.

Inhalation of toxic vapors, mists, gases, or dusts can produce poisoning by absorption through the mucous membrane of the mouth, throat, and lungs, and can seriously damage these tissues by local action. Inhaled gases or vapors may pass rapidly into the capillaries of the lungs and be carried into the circulatory system. This absorption can be extremely rapid. *Procedures involving volatile toxic substances and those operations involving solid or liquid toxic substances that may result in the generation of aerosols must be conducted in a hood or other suitable containment device.* The hood should have been evaluated previously to establish that it is providing adequate ventilation and has an average face velocity of not less than 80 linear ft/min. See Part IV-C for further discussion of the operation of laboratory hoods.

(4) Be prepared for accidents.

The laboratory worker should always be prepared for possible accidents or spills involving toxic substances. To minimize hazards from accidental breakage of apparatus or spills of toxic substances in the hood, containers of such substances should generally be stored in pans or trays made of polyethylene or other chemically resistant material and (particularly in large scale work) apparatus should be mounted above trays of the same type of material. Alternatively, the working surface of the hood can be fitted with a removable liner of adsorbent plastic-backed paper. Such procedures will contain spilled toxic substances in a pan, tray, or adsorbent liner and greatly simplify subsequent cleanup and disposal.

If a major release of a particularly hazardous substance occurs outside the hood, then the room or appropriate area should be evacuated and necessary measures taken to prevent exposure of other workers. The Industrial Hygiene Program should be contacted (253-2596) for assistance and equipment for spill clean-up; IHP personnel can be contacted for assistance after working hours by calling Campus Police (x 100). Spills should only be cleaned up by personnel wearing suitable personal protective apparel. If a spill of a toxicologically significant quantity of toxic material occurs outside the hood, a supplied-air full-face respirator should be worn. Contaminated clothing and shoes should be thoroughly decontaminated or incinerated. See Part V-C for further discussion of the control of accidental releases of toxic substances.

(5) Don't contaminate the environment.

Vapors that are discharged from experiments involving particularly hazardous substances should be trapped or condensed to avoid adding substantial quantities of toxic vapor to the hood exhaust air. The general waste disposal procedures outlined in Part V-C should be followed; however, certain additional precautions should be observed when waste materials are known to contain substances of moderate or high toxicity. Volatile toxic substances should never be disposed of by evaporation in the hood. If practical, *waste materials and waste solvents containing toxic substances should be decontaminated chemically by some procedure that can reasonably be expected to convert essentially all of the toxic substances to nontoxic substances* (for a discussion, see *Prudent Practices for Disposal of Chemicals from Laboratories*, pp. 56-100 and *Destruction of Hazardous Chemicals in the Laboratory* by G. Lunn and E. B. Sansone). If chemical decontamination is not feasible, the waste materials and solvents containing

toxic substances should be stored in closed, impervious containers so that personnel handling the containers will not be exposed to their contents. In general, liquid residues should be contained in glass or polyethylene bottles. All containers of toxic wastes should be suitably labeled to indicate the contents (chemicals and approximate amounts) and the type of toxicity hazard that contact may pose. For example, containers of wastes from experiments involving appreciable amounts of weak or moderate carcinogens should carry the warning: **CANCER SUSPECT AGENT**. All wastes and residues that have not been chemically decontaminated in the exhaust hood where the experiment was carried out should be disposed of in a safe manner that ensures that personnel are not exposed to the material.

(6) Recordkeeping.

Every research group in the department is required to maintain a list of all particularly hazardous substances in use in their laboratories. It is recommended that Group EHS Representatives be assigned the responsibility for ensuring that this inventory list is kept up to date. In addition, records that include amounts of material used and names of workers involved should be kept as part of the laboratory notebook record of all experiments involving particularly hazardous substances.

(7) Restrict access to areas where particularly hazardous substances are in use.

*Those operations involving particularly hazardous substances in which there is the possibility of the accidental release of harmful quantities of the toxic substance must be carried out in designated areas. As discussed in Part VI-B, in the Chemistry Department many laboratory hoods are **designated areas** for work with particularly hazardous substances. Designated areas should be posted with special warning signs indicating that particularly toxic substances may be in use.*

D. Additional Procedures for Working with Substances of Known High Chronic Toxicity

All of the procedures and precautions described in the preceding section should be followed when working with substances known to have high chronic toxicity. In addition, when such substances are to be used in quantities in excess of a few milligrams to a few grams (depending on the hazard posed by the particular substance), the additional precautions described below should also be used. A substance that has caused cancer in humans or has shown high carcinogenic potency in test animals (but for which a regulatory standard has not been issued by OSHA) will generally require the use of these additional procedures. However, this determination will also depend on other factors, such as the physical form and the volatility of the substance, the kind and duration of exposure, and the amount of material to be used. Besides strong carcinogens, substances in the high chronic toxicity category include potent reproductive toxins and certain heavy metal compounds such as dimethylmercury and nickel carbonyl. See Section VI-A for a more detailed discussion of the identification of substances with high chronic toxicity.

(1) Approvals.

Permission must be obtained from your research supervisor prior to any work with substances of known high chronic toxicity. It is the supervisor's responsibility to approve all plans for experimental operations and waste disposal. In addition, note that prior approval from the Chemistry Department EHS Committee is required for work with certain extremely hazardous substances (see Part VII).

(2) Restrict access to areas where substances of high chronic toxicity are being used and stored.

Any volatile substances having high chronic toxicity should be stored in a ventilated storage area in a secondary tray or container having sufficient capacity to contain the material should the primary container accidentally break. All containers of substances in this category should have labels that identify the contents and include a warning such as the following: WARNING! HIGH CHRONIC TOXICITY or CANCER SUSPECT AGENT. Storage areas for substances in this category should be designated areas (see Part VI-B), and special signs should be posted if a special toxicity hazard exists. With the exception of materials that require refrigeration, substances of high chronic toxicity should be stored in areas maintained under negative pressure with respect to surrounding areas (e.g., fume hoods).

All experiments with and transfers of such substances or mixtures containing such substances should be done in a designated area such as a suitably posted, efficient laboratory hood. When a negative-pressure glove box in which work is done through attached gloves is used, the ventilation rate in the glove box should be at least two volume changes per hour, the pressure should be at least 0.5 in. of water lower than that of the external environment, and the exit gases should be passed through a trap or HEPA filter. Positive-pressure glove boxes are normally used to provide an inert anhydrous atmosphere. If these glove boxes are used with highly toxic compounds, then the box should be thoroughly checked for leaks before each use and the exit gases should be passed through a suitable trap or filter. Laboratory vacuum pumps used with substances having high chronic toxicity should be protected by high-efficiency scrubbers or HEPA filters and vented into an exhaust hood. Motor-driven vacuum pumps are recommended because they are easy to decontaminate. (Note: decontamination of a vacuum pump should be carried out in an exhaust hood). Designated areas should be clearly marked with a conspicuous sign reading: DESIGNATED AREA FOR USE OF PARTICULARLY HAZARDOUS SUBSTANCES — AUTHORIZED PERSONNEL ONLY. Only authorized and instructed personnel should be allowed to work in or have access to such designated areas.

(3) Wear suitable protective apparel.

Proper gloves should be worn when transferring or otherwise handling substances or solutions of substances having high chronic toxicity. Two gloves should generally be worn on each hand. In the event of an accident, the outer, contaminated gloves can then be removed and the researcher can immediately take steps to deal with the accident. To avoid contamination of the general laboratory environment, protective gloves should be removed when leaving a designated area (e.g. to answer the telephone). In some cases, the laboratory worker or the research supervisor may deem it advisable to use other protective apparel such as an apron of reduced permeability covered by a disposable coat. Extreme precautions such as these might be taken, for example, when handling large amounts of certain heavy metals and their derivatives or compounds known to be potent carcinogens. After working with such substances, laboratory workers should remove any protective apparel that has been used and thoroughly wash hands, forearms, face, and neck

(4) Protect the environment and dispose of waste materials properly.

Surfaces on which high-chronic-toxicity substances are handled should be protected from contamination by using chemically resistant trays or pans that can be decontaminated after the experiment or by using dry, absorbent, plastic-backed paper that can be disposed of after use.

Wastes and other contaminated materials from an experiment involving substances of high chronic toxicity should be collected together with the washings from flasks and such and either decontaminated chemically or placed in closed, suitably labeled containers for eventual incineration. If chemical decontamination is to be used, a method should be chosen that can reasonably be expected to convert essentially all of the toxic materials into nontoxic materials. For example, residues and wastes from experiments in which beta-propiolactone, bis(chloromethyl)ether, or methyl chloromethyl ether have been used should be treated for 10 min with concentrated aqueous ammonia. In the event that chemical decontamination is not feasible, wastes and residues should be placed in an impervious container that should be closed and labeled in some manner such as the following: CAUTION: COMPOUNDS OF HIGH CHRONIC TOXICITY or CAUTION: CANCER SUSPECT AGENT. In general, liquid wastes containing such compounds should be placed in glass or (usually preferable) polyethylene bottles and these should be transported in plastic or metal pails of sufficient capacity to contain the material in case of accidental breaking of the primary container. Consult the Environmental Management Program for instructions on the disposal of contaminated waste materials.

Normal laboratory work should not be resumed in an area that has been used for work with substances of high chronic toxicity until it has been adequately decontaminated. Work surfaces should be thoroughly washed and rinsed. If experiments have involved the use of finely divided solid materials, dry sweeping should not be done. In such cases, surfaces should be cleaned by wet mopping or by use of a vacuum cleaner equipped with a high efficiency particulate air (HEPA) filter. All equipment (e.g., glassware, vacuum traps, and containers) that is known or suspected to have been in contact with substances of high chronic toxicity should be washed and rinsed before they are removed from the designated area.

(5) Be prepared for accidents.

Be prepared for the release of a substance of high chronic toxicity by formulating a contingency plan to deal with any accident which may occur. The EHS Office (N52-496, 452-3477) can provide assistance in preparing these contingency plans. Make sure that the necessary equipment and materials are on hand to deal with possible accidents before beginning work with substances of high chronic toxicity.

(6) Medical Surveillance.

If you anticipate being involved in continued experimentation with a substance of high chronic toxicity (i.e., if you regularly use toxicologically significant quantities of such a substance three times a week), then a qualified physician should be consulted to determine whether it is advisable to establish a regular schedule of medical surveillance or biological monitoring. See Part IX for a further discussion of medical surveillance.

E. Special Handling Procedures for Some Common Particularly Hazardous Substances

This section outlines special handling procedures for some specific compounds that may be classified as particularly hazardous substances as they are used in Chemistry Department laboratories. The information presented in this section is not meant to be complete, and researchers should consult the appropriate literature and their laboratory supervisor before working with these particularly hazardous substances.

(1) Acrylonitrile

Acrylonitrile is regulated as a probable human carcinogen by OSHA and also is listed as a substance with a moderate degree of acute toxicity (oral LD₅₀ (rat) is 78 mg/kg). The PEL (permissible exposure limit) is 2 ppm; the TLV-TWA (threshold limit value – time-weighted average) is also 2 ppm. Acrylonitrile is severely irritating to the eyes and mildly irritating to the skin; prolonged contact with the skin can lead to burns. Acrylonitrile is a highly flammable liquid; its vapor forms explosive mixtures with air. *Work involving significant quantities of acrylonitrile should be conducted using the general procedures outlined in both Parts VI-C and VI-D.* In particular, work with acrylonitrile should be conducted in a fume hood to prevent exposure by inhalation; splash goggles and impermeable gloves should be worn at all times to prevent eye and skin contact.

(2) Benzene

Exposure to benzene can lead to both chronic as well as acute toxic effects. The acute toxic effects from skin contact, inhalation, or ingestion of benzene are low. In humans, acute inhalation exposure to benzene can produce a picture of acute delirium, characterized by excitement, euphoria, and restlessness and, if the exposure is significantly high, the symptoms may progress to depression, drowsiness, stupor, and even unconsciousness. The concentration required to produce this symptom complex is 1000 ppm or higher. These concentrations will also produce irritation of the eye, nose, and respiratory tract.

Chronic inhalation exposure to 25–50 ppm of benzene can produce changes in the blood picture that include macrocytosis, decrease in the total red blood count, decrease in platelets, decrease in the hemoglobin concentration, or decrease in leukocytes. Any or all of these hematologic effects may be seen in any individual. Usually, the worker will be asymptomatic while these effects are observed in the blood picture. Continued exposure at somewhat higher concentrations (probably more than 100 ppm) can insidiously result in more severe blood disorders that include leukopenia or even aplastic anemia, with symptoms of headaches, dizziness, loss of appetite, nervousness, irritability, and perhaps bleeding manifestations, i.e., nosebleeds, easy bruisability, or hematuria. Severe cases may have fatal outcomes. Recently, a number of reports have been published that describe leukemia in workers who have had aplastic anemia. These cases have been reported in Italy and Turkey in workers exposed to grossly high concentrations of benzene. In addition, there is some indication that an excess of leukemia may occur without a preceding picture of aplastic anemia in workers who have been repeatedly exposed to benzene at concentrations of more than 100 ppm.

The current OSHA PEL (permissible exposure limit) for benzene is 1 ppm as an 8-hour time-weighted average (TWA), 25 ppm for a ceiling concentration for time period such that the 8-hour TWA is not exceeded, and a peak above the ceiling of 50 ppm for no more than 10 min. The ACGIH TLV-TWA value is 10 ppm. Benzene is a flammable liquid and should not be exposed to heat or flame. An explosion hazard also exists when its vapors are exposed to flame. Benzene may react vigorously with oxidizing agents such as bromine pentafluoride, chlorine, chromic acid, nitryl

perchlorate, oxygen, ozone, perchlorates, aluminum chloride plus fluorine perchlorate, sulfuric acid plus permanganates, potassium peroxide, silver perchlorate plus acetic acid, and sodium peroxide.

Experiments involving the use of significant quantities of benzene should be conducted employing the general procedures outlined in Part VI-C; all operations in which there is the possibility of the accidental release of harmful quantities of benzene should be carried out in a designated area.

(3) Bis(chloromethyl)ether (BCME), Chloromethyl Methyl Ether, and Other Chloromethyl Ether Derivatives

Because of the high volatility of bis(chloromethyl)ether (BCME), inhalation is the route of exposure that presents the greatest hazard to humans. BCME vapor is severely irritating to the skin and mucous membranes and can cause corneal damage that heals slowly. The substance has caused lung cancer in humans. BCME is highly toxic to animals via inhalation: LD₅₀ (rats, 7-hour inhalation) = 7 ppm. It is moderately toxic via the oral and skin routes: LD₅₀ (rats, oral) = 280 mg/kg; LD₅₀ (rabbits, skin) = 368 mg/kg. Its vapors are strongly irritant to the eyes of rats. Rats and hamsters subjected to 10 or 30 6-hour exposures of 1 ppm BCME showed evidence of tracheal and bronchial hyperplasia, as well as effects on the central nervous system. BCME is carcinogenic to mice following inhalation, skin application, or subcutaneous administration. In newborn mice, it is carcinogenic by inhalation and subcutaneous administration. BCME is a lung carcinogen in humans.

The TLV (threshold limit value) for BCME is 0.001 ppm (1 ppb; 5 mg/m³). The substance is classified by ACGIH as a human carcinogen. OSHA has classified BCME as a cancer-suspect agent and has stringent regulations (29 CFR 1910.1008) for its use if its concentration in a material exceeds 0.1%. *Work involving chloromethyl ether derivatives must be carried out using the general procedures outlined in Parts VI-C and VI-D.*

(4) Carbon Monoxide

Carbon monoxide is a direct and cumulative poison. It combines with the hEMPGlobin of the blood to form a relatively stable compound (carboxyhemoglobin) rendering it useless as an oxygen carrier. When about one-third of the hemoglobin has entered into such combination, the victim dies. Since carbon monoxide is odorless, colorless, and tasteless, it has no warning properties. Exposure to 1500–2000 ppm CO in air for 1 hour is dangerous, and exposure to 4000 ppm is fatal in less than 1 hour. Headache and dizziness are the usual symptoms of CO poisoning, but occasionally the first evidence of poisoning is the collapse of the patient. Pregnant women are more susceptible to the effects of carbon monoxide exposure.

Carbon monoxide should be used only in areas with adequate ventilation employing the general procedures outlined in Part VI-C. A trap or vacuum break should always be used to prevent impurities from being sucked back into a CO cylinder.

(5) Carbon Tetrachloride

The current OSHA PEL (permissible exposure limit) and ACGIH TLV (threshold limit value) for carbon tetrachloride are 2 ppm as an 8-hour time-weighted average and 5 ppm as a ceiling for any period of time provided the 8-hour average is not exceeded. ACGIH states that skin contact may account for a substantial part of toxic responses.

The acute toxicity of carbon tetrachloride by all routes of exposure is low to moderate (oral LD₅₀ in rats is 2,350 mg/kg). Carbon tetrachloride shows carcinogenic effects in animal studies and is listed in group 2B (“possible human carcinogen”) by IARC. *In most of its uses in Chemistry Department*

laboratories it need not be treated as a particularly hazardous substance. In cases where large quantities of carbon tetrachloride are in frequent use, then the general procedures outlined in Part VI-C should provide adequate protection. All operations should be carried out in a hood, not only because of the carcinogenicity of the substance, but also because of its other toxic effects (e.g., hepatotoxicity) and its volatility. Nitrile rubber is the recommended material for gloves and other protective clothing.

(6) Chlorine

Chlorine is a severe irritant of the eyes, skin, and mucous membranes. Inhalation may cause coughing, choking, nausea, vomiting, headache, dizziness, difficulty breathing, and delayed pulmonary edema which can be fatal. Exposure to *ca.* 500 ppm for 30 minutes may be fatal and 1000 ppm can be lethal after a few breaths. Chlorine is highly irritating to the eyes and skin; exposure to 3–8 ppm causes stinging and burning of the eyes, and contact with liquid chlorine or high concentrations of the vapor can cause severe burns. Chlorine can be detected by its odor below the permissible limit; however, because of olfactory fatigue, odor may not always provide adequate warning of the presence of harmful concentrations of this substance. There is no evidence for carcinogenicity or reproductive or developmental toxicity of chlorine in humans. The LC₅₀ for inhalation (rat) is 293 ppm (1 h); the PEL (permissible exposure limit) is 1 ppm while the TLV-TWA (threshold limit value – time-weighted average) is 0.5 ppm.

Chlorine is noncombustible but is a strong oxidizer and will support combustion of most flammable substances, sometimes with explosive violence. Cylinders of chlorine should be stored in locations appropriate for compressed gas storage and separated from incompatible compounds such as hydrogen, acetylene, ammonia, and flammable materials. Because of its high toxicity, *laboratory operations using chlorine must be carried out in a hood employing the general procedures outlined in Part VI-C.*

(7) Chloroform

The acute toxicity of chloroform is classified as moderate by ingestion and low by inhalation. Inhalation exposure to chloroform at concentrations greater than 1000 ppm can produce dizziness, nausea, and headaches. At higher concentrations, there can be disorientation and delirium progressing to unconsciousness. Such high exposure can also produce liver and possibly kidney damage. It is believed that chloroform can sensitize the heart to adrenaline, so it may cause cardiac arrhythmias and possibly death. High concentrations of the vapor can produce conjunctivitis. Liquid chloroform in the eyes will produce a painful corneal injury that usually heals in several days.

Chronic exposure to chloroform at concentrations of 100–200 ppm has been reported to produce large livers. Continued contact with the skin can produce drying, fissuring, and inflammation. In experimental studies, prolonged ingestion of high levels of chloroform by mice resulted in liver cancers and by rats, kidney tumors. Chloroform has produced embryo toxicity in experimental animals. It is a suspected human carcinogen.

Although the fire hazard of chloroform is slight, exposure to heat or flame can result in generation of phosgene gas. Chloroform reacts violently with acetone in the presence of base, and with aluminum, disilane, lithium, magnesium, nitrogen tetroxide, potassium, perchloric acid plus phosphorus pentoxide, potassium hydroxide plus methanol, potassium tert-butoxide, sodium, sodium hydroxide plus methanol, sodium methylate, and sodium hydride.

The current OSHA PEL (permissible exposure limit) for chloroform is 50 ppm as an 8-hour time-weighted average. This standard is also a ceiling level that should not be exceeded for any 15-min

period. The ACGIH currently recommends that chloroform be treated as a suspect human carcinogen and recommends an 8-hour time weighted average exposure of 10 ppm.

Although chloroform has caused tumors in animals, its potency is low. *In most of its uses in the Chemistry Department it need not be treated as a particularly hazardous substance.* In cases where significant quantities of chloroform are in frequent use, the general procedures outlined in Part VI-C should provide adequate protection. The high volatility of chloroform emphasizes the importance of a hood for such operations. Polyvinyl alcohol gloves provide the best hand protection.

(8) Dimethyl and Diethyl Sulfate

Many cases of dimethyl sulfate poisoning have been reported. The common initial symptoms are headache and giddiness, with burning of the eyes. The patient's condition may worsen, with painful eyes, nose and throat irritation, loss of voice, coughing, difficulty in breathing and swallowing, vomiting, and diarrhea possible. The onset of the symptoms may be delayed up to 10 hours. This substance is extremely hazardous because of its lack of warning properties and its delayed toxic effects. Skin contact causes blistering and necrosis, and DMS can be absorbed through the skin in sufficient quantity to cause systemic intoxication. In the worst cases, there is severe inflammation of the mucous membranes and pulmonary injury that may be fatal; several deaths have occurred. For example, exposure to 97 ppm for 10 min was fatal. DMS is moderately toxic to animals via the oral route: LD₅₀ (rats) = 440 mg/kg. Undiluted DMS produced moderate to severe irritation when applied to the skin of guinea pigs; 1% DMS produced mild irritation. DMS does not cause skin sensitization in animals. Undiluted DMS applied to rabbit eyes produced severe injury. Even a 1-hour exposure to 58 ppm has resulted in permanent eye damage in rats. During a 4-hour exposure, 30 ppm DMS killed five out of six rats, but 15 ppm was not lethal.

DMS has been shown to be carcinogenic in the rat by inhalation, subcutaneous injection, and following 1 hour per day exposures to 10 ppm DMS for 130 days. The TLV (threshold limit value) for DMS is 0.1 ppm (0.5 mg/m³) as an 8-hour time-weighted average. DMS is classified as being suspected of carcinogenic potential in humans by the ACGIH. The OSHA PEL (permissible exposure limit) for DMS is 1.0 ppm. These limits include a warning of the potential contribution of skin absorption to the overall exposure.

The general procedures outlined in Part VI-D should be used when handling more than a few grams of DMS in view of its fairly high carcinogenic potency in rats by inhalation and its ability to penetrate the skin. It is particularly important to avoid skin contact by the appropriate use of rubber gloves, a rubber apron, and other protective apparel, and to avoid inhalation of even low concentrations of vapor by working in a hood. Operations involving smaller quantities of DMS can be conducted using the general procedures presented in Part VI-C.

(9) Ethylene Dibromide (1,2-Dibromoethane)

Ethylene dibromide (EDB) is classified as a compound with a moderate degree of acute toxicity; the approximate oral lethal dose of EDB for humans is 5-10 mL. Skin absorption of EDB can also cause death, and inhalation of the vapor can produce pulmonary edema. EDB can cause severe irritation to all exposed tissues, respiratory tract, skin, and eye. Systemic effects include central nervous system depression, kidney injury, and severe liver necrosis. Ethylene dibromide is highly toxic to animals via inhalation. The maximum survival exposure of rats to EDB vapors in air are 3000 ppm for 6 min, 400 ppm for 30 min, and 200 ppm for 2 hours. It is moderately toxic via the oral and skin routes: LD₅₀ (rats, oral) = 108 mg/kg; LD₅₀ (rabbits, skin) = 300 mg/kg. EDB is markedly irritating to skin, and a 10% solution has caused serious but reversible corneal injury in rabbit eyes.

Rats were repeatedly exposed to 50 ppm EDB for 6 months. Half died from pneumonia and upper respiratory tract infections. Slight changes in the liver and kidney were seen. EDB has induced a high incidence of tumors (squamous-cell carcinomas of the forestomach) in mice and rats following oral administration. The 1979 TLV (threshold limit value) for EDB was 20 ppm (155 mg/m³) as an 8-hour time-weighted average. The exposure limit is 30 ppm over any 15-min period. These limits include a warning about the potential contribution of skin absorption to the overall exposure. In 1980, the ACGIH put EDB in category A 1b (human carcinogen). For this category, there is no assigned TLV (threshold limit value), but the ACGIH recommends that those working with A1b carcinogens should be properly equipped to ensure virtually no contact with the carcinogens. The OSHA PEL (permissible exposure limit) for EDB is 20 ppm, and the acceptable maximum peak is 50 ppm for 5 min in any 8-hour time period.

On the basis of the carcinogenicity data for EDB, *the procedures described in Part VI-D should be followed when handling more than a few grams in the laboratory.* Operations involving smaller quantities can be carried out using the procedures outlined in Part VI-C. Serious skin injury can occur from direct exposure to EDB. The substance can penetrate neoprene and several other types of plastic; therefore, gloves and other protective apparel made of these materials provide only temporary protection if EDB spills on them.

(10) Hydrazine

Hydrazine is classified as a compound with a high degree of acute toxicity; exposure to its vapors can cause respiratory tract irritation, excitement, convulsion, cyanosis, and decrease in blood pressure. The liquid can severely burn the eyes and skin. Hydrazine can cause fatty degeneration of the liver, nephritis, and hemolysis. Hydrazine also poses a dangerous fire and explosion risk and can explode during distillation if traces of air are present. Hydrazine is moderately toxic to animals via the inhalation, oral, and skin routes: LC₅₀ (rats, 4-hour inhalation) = 570 ppm; LD₅₀ (rats, oral) = 60 mg/kg; LD₅₀ (rabbits, skin) = 283 mg/kg (hydrazine hydrate). It is a strong skin and mucous membrane irritant and a strong skin sensitizer. Hydrazine hydrate produced moderately severe irritation when applied to rabbit eyes. After repeated oral, skin, or injection exposure, the effects noted include weight loss, weakness, vomiting, and convulsions. The chief histological finding is fatty degeneration of the liver. Among guinea pigs and dogs exposed to hydrazine in the air 5–47 times, the dogs showed liver damage, with lesser damage to the kidneys and lungs, while the guinea pigs had pneumonitis and partial lung collapse. Hydrazine is not regarded as having adequate warning properties.

Hydrazine and hydrazine salts have been shown to be carcinogenic in mice after oral and intraperitoneal administration and in rats following oral dosing. By the oral route, effects were found at doses of 24–36 (mg/kg)/day in mice and 20 (mg/kg)/day in rats. No tumors were observed in Syrian golden hamsters after oral administration. The ACGIH has classified hydrazine as suspected of carcinogenic potential in humans. The TLV (threshold limit value) for hydrazine is 0.1 ppm (0.1 mg/m³) and the OSHA PEL (permissible exposure limit) is 1.0 ppm (1 mg/m³) as 8-hour time-weighted averages. These limits include a warning about the potential contribution of skin absorption to the overall exposure. NIOSH has (1978) recommended a ceiling limit of 0.03 ppm in any 2-hour period.

When more than a few grams of hydrazine are to be used in the laboratory, the general procedures outlined in both Parts VI-C and VI-D should be used because hydrazine is carcinogenic in animal tests, quite volatile, and readily absorbed through the skin. Nitrile rubber is recommended for gloves and other protective apparel. Prompt washing with water effectively removes hydrazine from skin that it has splashed on. Hydrazine should not be used in the vicinity of a flame or under conditions where sparks can occur, as an explosion or fire can result.

(11) Hydrogen Bromide and Hydrogen Chloride

Both hydrogen bromide (HBr) and hydrogen chloride (HCl) are toxic gases which are severely irritating to the upper respiratory tract. The acids formed neutralize the alkali of the tissues and can cause death as a result of edema or spasm of the larynx and inflammation of the upper respiratory system. Concentrations of 0.13–0.2% are lethal for human beings in exposures lasting a few minutes. However, because of their odor, usually these gases provide adequate warning for prompt voluntary withdrawal from contaminated atmospheres. These gases are also corrosive to the skin and mucous membranes and can cause severe burns. Exposure to high concentrations may also result in dermatitis. Contact with the eyes rapidly causes severe irritation of the eyes and eyelids.

Hydrogen bromide and hydrogen chloride are corrosive gases that have pungent, irritating odors, detectable at 2 ppm for HBr and at 0.25–10 ppm for HCl. The OSHA PEL for HBr is 3 ppm and is 5 ppm for HCl. The irritating odor of these substances provides adequate warning. Although both are colorless, they fume in moist air because of their high solubility in water. In a cylinder under pressure, both exist in the form of a gas over a liquid (under such conditions, the cylinder pressure is equal to the vapor pressure of the substance contained; at 25°C, this is 4.22 MPa (613 lb/in.²) for HCl and 2.20 MPa (320 lbf/in.²) for HBr). As long as liquid is present in the cylinder, the pressure will remain fairly constant. Although neither HBr nor HCl is combustible, both react with common metals to form hydrogen, which may form explosive mixtures with air.

Operations involving significant quantities of hydrogen bromide and hydrogen chloride should be conducted using the general procedures outlined in Part VI-C. Laboratory workers should wear protective apparel, including rubber gloves, suitable gas-tight chemical safety goggles, and clothing such as a rubber or plastic apron. Proper respiratory equipment should be available. These gases should be handled only in adequately ventilated areas. A check valve, vacuum break, or trap should always be used to prevent foreign materials from being sucked back into the cylinder because this can cause the development of dangerous pressures. Leaks of HBr or HCl will be evident by the formation of dense white fumes on contact with the atmosphere. Small leaks of HCl can be detected by holding an open bottle of concentrated ammonium hydroxide near the site of the suspected leak; the formation of dense white fumes confirms the existence of a leak. Cylinder-valve leaks can usually be corrected by tightening the valve packing nut (by turning it clockwise as viewed from above).

(12) Hydrogen Cyanide

Prior approval from the Chemical Hygiene Committee is required before using hydrogen cyanide (see Part VII).

(13) Hydrofluoric Acid

The use of anhydrous hydrogen fluoride requires prior approval from the Chemical Hygiene Committee. All forms — dilute or concentrated solutions or the vapor — of hydrofluoric acid (HF) cause severe burns. Inhalation of anhydrous HF or HF mist or vapors can cause severe respiratory tract irritation that may be fatal. Death from pulmonary edema occurred within 2 hours in three of six workers splashed with 70% HF solution despite prompt showering with water. Anhydrous HF is a clear, colorless liquid that boils at 19.5°C. Because of its low boiling point and high vapor pressure, anhydrous HF must be stored in pressure containers. A 70% aqueous solution is a common form of HF. Hydrofluoric acid is miscible with water in all proportions and forms an azeotrope (38.3% HF) that boils at 112°C. Anhydrous or concentrated aqueous HF causes immediate and serious burns to any part of the body. Dilute solutions (<30%) and gaseous HF are also harmful, although several hours may pass before redness or a burning sensation is noticed. These burns may still be quite severe and progressively damaging to the skin and deeper tissues. “Undissociated HF readily

penetrates skin and deep tissue where the corrosive fluoride ion can cause necrosis of soft tissues and decalcification of bone; the destruction produced is excruciatingly painful. Fluoride ion also attacks enzymes (e.g. of glycolysis) and cell membranes. The process of tissue destruction and neutralization of the hydrofluoric acid is prolonged for days, unlike other acids that are rapidly neutralized. Because of the insidious manner of penetration, a relatively mild or minor exposure can cause a serious burn” [Proctor, N. H.; Hughes, J. P.; Fischman, M. L. *Chemical Hazards of the Workplace*, J. B. Lippincott Co., Philadelphia, 1988, p. 279]. Occasionally workers fail to recognize the importance of seeking medical attention for HF burns *before* pain commences. By the time the victim is affected with progressively deep and more painful throbbing and burning, serious damage may have taken place. Exposures under fingernails can be a particularly painful problem if ignored. Wearing clothing (including leather shoes and gloves) that has absorbed small amounts of HF can result in serious delayed effects such as painful slow-healing skin ulcers.

When handling HF, it is crucial to ensure adequate ventilation by working only in a hood so that safe levels (3 ppm) are not exceeded. All contact of the vapor of the liquid with eyes, skin, respiratory system, or digestive system must be avoided by using protective equipment such as a face shield and neoprene or polyvinyl chloride gloves. The protective equipment should be washed after each use to remove any HF on it. Safety showers and eyewash fountains should be nearby. Anyone working with HF should have received prior instructions about its hazards and in proper protective measures and should know the recommended procedure for treatment in the event of exposure (Reinhardt, C.F. et al.; *Am. Ind. Hyg. Assn. J.*, 1966, 27, 166).

Spills and leaks — The vapors of both anhydrous HF and aqueous 70% HF produce visible fumes if they contact moist air. This characteristic can be useful in detecting leaks but cannot be relied on because of atmospheric variations. Spills of HF must be treated immediately to minimize the dangers of vapor inhalation, body contact, corrosion of equipment, and possible generation of hazardous gases. Spills should be contained and diluted with water. The resulting solution should be neutralized with lime before disposal.

Waste disposal — Waste HF should be slowly added to a larger volume of a stirred solution of slaked lime to precipitate calcium fluoride, which is chemically inert and poses little toxic hazard (sodium fluoride is highly soluble and toxic). Alternatively, hydrofluoric acid can be diluted to about 2% concentration with cold water in a polyethylene vessel, neutralized with aqueous sodium hydroxide, and treated with excess calcium chloride solution to precipitate calcium fluoride.

In the event of exposure — Anyone who knows or even suspects that he or she has come into direct contact with HF should immediately flush the exposed area with large quantities of cool water. Exposed clothing should be removed as quickly as possible while flushing. Medical attention should be obtained promptly, even if the injury appears slight. On the way to the physician, the burned area should be immersed in a mixture of ice and water. If immersion is impractical, a compress made by inserting ice cubes between layers of gauze should be used. Make sure that the physician understands that the injury was caused by HF and requires treatment very different from other acid burns. Even in the case of very small exposure, washing alone may not be sufficient to completely prevent injury. For minor exposures such as small hole in a glove, application of a calcium gluconate antidote gel can bind free fluoride ion not removed by washing. For regular HF users, this gel may be obtained by contacting the EHS Office (452-3477). Be sure to closely check/monitor the expiration date on the tube of calcium gluconate antidote gel, as it has a relatively short shelf life.

If HF liquid or vapor has contacted the eyes, these organs should be flushed with large quantities

of clean water while the eyelids are held apart. This flushing should be continued for 15 minutes. Medical attention should be obtained promptly.

Anyone who has inhaled HF vapor should be removed immediately to an uncontaminated atmosphere and kept warm. Medical help should be obtained promptly. Anyone who has ingested HF should drink a large quantity of water as quickly as possible. Do not induce vomiting. Again, medical help should be obtained promptly. After the acid has been thoroughly diluted with water, if medical attention is delayed, the person should be given milk or two fluid ounces of milk of magnesia to drink to soothe the burning effect.

(14) Hydrogen Sulfide

The acute toxicity of hydrogen sulfide by inhalation is moderate. A five minute exposure to 800 ppm has resulted in death. Inhalation of 1000 to 2000 ppm may cause coma after a single breath. Exposure to lower concentrations may cause headache, dizziness, and nausea. Low concentrations (20-150 ppm) of hydrogen sulfide can cause eye irritation which may be delayed in onset. Although the odor of hydrogen sulfide is detectable at very low concentrations (below 0.1 ppm), it rapidly causes olfactory fatigue at higher levels, and therefore is not considered to have adequate warning properties. Hydrogen sulfide has not been shown to be carcinogenic or to have reproductive or developmental effects in humans. The hydrogen sulfide LC₅₀ for inhalation (rat) is 444 ppm; the PEL (permissible exposure limit) *ceiling* is 20 ppm, and the TLV-TWA (threshold limit value - time-weighted average) is 10 ppm. Hydrogen sulfide is flammable in air, and the combustion products are also toxic by inhalation. It is incompatible with strong oxidizers, will attack many metals, some plastics and rubbers, and reacts violently with a variety of metal oxides. *Laboratory operations with hydrogen sulfide should be carried out in a hood using the general procedures outlined in Part VI-C.* In particular, cylinders of hydrogen sulfide should be stored and used in a continuously ventilated gas cabinet or fume hood.

(15) Nickel Carbonyl

The use of nickel carbonyl requires prior approval from the Chemistry Department Chemical Hygiene Committee (see Part VII).

(16) Nitrogen Dioxide

Nitrogen dioxide (NO₂) is classified as a highly acute toxin; it is a primary irritant, acting principally on the lungs and to a lesser extent on the upper respiratory tract. It is certainly one of the most insidious of the gases. The inflammation of the lungs may cause only slight pain, but the edema that results may easily cause death. Toxic effects may develop after a 10 minute exposure to 10 ppm, and one hundred ppm of NO₂ in air is a dangerous concentration for even a short exposure. Exposure to 200 ppm for 1-2 min may be fatal.

Nitrogen dioxide gas is reddish brown, has an irritating odor, and must be avoided by the use of an air-purifying respirator equipped with an acid-gas cartridge or canister; at concentrations greater than 50 times the TLV (threshold limit value), a positive-pressure atmosphere-supplying respirator must be used and, in IDLH atmospheres, a pressure-demand self-contained breathing apparatus or a positive-pressure air-line respirator that has escape-cylinder provisions is required.

Nitrogen dioxide should be handled using the general procedures outlined in Part VI-C. Nitrogen dioxide is a deadly poison, and no one should work with a cylinder of this substance unless they are fully familiar with its handling and its toxic effect. Ventilation is extremely important, and respiratory protective equipment should always be available. Only stainless steel fittings should be used.

(17) Mercury

The element mercury is a liquid metal with a vapor pressure of 0.00185 mm at 25°C. This corresponds to a saturation concentration of 20 milligrams of mercury per cubic meter of air or 2.4 parts per million of air. The American Conference of Governmental Industrial Hygienists has established a threshold limit for mercury vapor of 0.05 milligrams of mercury per cubic meter of air for continuous 40-hour per week exposure. Long term chronic exposure to mercury vapor in excess of 0.05 mg of mercury per cubic meter of air may result in cumulative poisoning. The use of mercury in laboratory amounts in well-ventilated areas is fairly safe; however special precautions must be followed when working with large quantities of mercury.

Mercury poisoning from exposure by chronic inhalation produces a variety of symptoms. The characteristic effects are emotional disturbances, unsteadiness, inflammation of the mouth and gums, general fatigue, memory loss, and headaches. Kidney damage may result from poisoning by mercurical salts. In most cases of exposure by chronic inhalation, the symptoms of poisoning gradually disappear when the source of exposure is removed. However, improvement may be slow and complete recovery may take years. Skin contact with mercury compounds produces irritation and various degrees of corrosion. Soluble mercury salts can be absorbed through the intact skin and produce poisoning.

The general procedures outlined in Part VI-C should be followed when working with large quantities of liquid mercury. Every effort should be made to prevent spills of metallic mercury because the substance is extremely difficult and time consuming to pick up. Droplets get into cracks and crevices, under table legs, and under and into equipment. If spills are frequent and Hg is added to the general air level, the combined concentration may exceed the allowable limits.

Storage — Containers of large quantities of mercury should be kept closed and stored in secondary containers in a well-ventilated area. When breakage of instruments or apparatus containing mercury is a possibility, the equipment should be placed in an enameled or plastic tray or pan that can be cleaned easily and is large enough to contain the mercury in the event of accident. Transfers of Hg from one container to another should be carried out in a hood, over a tray or pan to confine any spills.

Clean Up of spills — Pools of metallic Hg can be collected by suction by using an aspirator bulb or a vacuum device made from a filtering flask, a rubber stopper, and several pieces of flexible rubber and glass tubing. Alternatively, mercury-spill cleanup kits are available commercially. When a large spill, pressure system rupture, or heating of mercury is involved, the EHS Office (452-3477) will be glad to survey the area and advise on the degree of hazard which may exist and necessary preventive measures to be undertaken. A special “mercury vacuum cleaner” may be borrowed from the Industrial Hygiene Program (253-2596) for use in cleaning up large spills. If Hg has spilled on the floor, the workers involved in cleanup and decontamination activities should wear plastic shoe covers. When the cleanup is complete, the shoe covers should be disposed of and the workers should thoroughly wash their hands, arms, and face several times.

Waste Disposal — Significant quantities of metallic Hg from spills or broken thermometers or other equipment, and contaminated Hg from laboratory activities should be collected in thick-walled high-density polyethylene bottles for reclamation. Rags, sponges, shoe covers, and such used in cleanup activities, and broken thermometers containing small amounts of residual mercury, should be placed in a sealed plastic bag, labeled, and disposed of as hazardous waste.

(18) N-Nitrosodialkylamines and Certain Other N-Nitroso Compounds

N-Nitrosodimethylamine is strongly hepatotoxic and can cause death from liver insufficiency in experimental animals. It is carcinogenic in at least 10 animal species, and is regarded to be a probable human carcinogen. The main targets for its carcinogenic activity are the liver, lung, esophagus, trachea, and nasal cavity. Although data are not available on the toxicity of N-nitrosodiethylamine in humans, the closely related compound N-nitrosodimethylamine has caused extensive liver damage as a consequence of ingestion, inhalation, or topical application to the skin. It is prudent to regard other nitrosamine derivatives as being potential carcinogens.

The general procedures outlined in Parts VI-C and Part VI-D should be followed when working with N-nitrosodialkylamines. All work with N-nitrosodialkylamines should be carried out in a well-ventilated hood or in a glove box equipped with a HEPA filter. To the extent possible, all vessels that contain N-nitrosodialkylamines should be kept closed. All work should be carried out in apparatus that is contained in or mounted above unbreakable pans that will contain any spill. All containers should bear a label such as the following: CANCER-SUSPECT AGENT. All personnel who handle the material should wear plastic, latex, or neoprene gloves and a fully buttoned laboratory coat.

Storage — All bottles of N-nitrosodialkylamines should be stored and transported within an unbreakable outer container; storage should be in a ventilated storage cabinet (or in a hood).

Clean Up of spills and waste disposal — Because N-nitrosodialkylamines are chemically stable under usual conditions, disposal is best carried out by incineration. Contact the Environmental Management Office to arrange for the disposal of waste and contaminated materials. For incineration of liquid wastes, solutions should be neutralized if necessary, filtered to remove solids, and put in closed polyethylene containers for transport. All equipment should be thoroughly rinsed with solvent, which should then be added to the liquid waste for incineration. Great care should be exercised to prevent contamination of the outside of the solvent container. If possible, solid wastes should be incinerated; if this is not possible, solid wastes from reaction mixtures that may contain N-nitrosodialkylamines should be extracted and the extracts added to the liquid waste. Similarly, any rags, paper and such that may be contaminated should be incinerated. Contaminated solid materials should be enclosed in sealed plastic bags that are labeled CANCER-SUSPECT AGENT and with the name and amount of the carcinogen. The bags should be stored in a well-ventilated area until they are incinerated. Spills of N-nitrosodialkylamines can be absorbed by Celite R or a commercial spill absorbant. After the absorbant containing the major share of the nitrosamine has been picked up (avoid dusts; do not sweep), the surface should be thoroughly cleaned with a strong detergent solution. If a major spill occurs outside of a ventilated area, the room should be evacuated, the EHS Office (452-3477) should be contacted, and the cleanup operation should be carried out by persons equipped with self-contained respirators. Those involved in this operation should wear rubber gloves, laboratory coats, and plastic aprons or equivalent protective apparel.

(19) Phosgene

Phosgene is classified as a substance with a high degree of acute toxicity. In humans, the symptoms of overexposure to phosgene are dryness or a burning sensation in the throat, numbness, vomiting, and bronchitis. An airborne concentration of 5 ppm may cause eye irritation and coughing in a few minutes. The substance can cause severe lung injury in 1-2 min at a level of 20 ppm. Exposure to concentrations above 50 ppm is likely to be fatal. Phosgene is extremely toxic to animals via inhalation. Thus, 74% of a group of rats died from exposure to 55-100 ppm for only 10 min. Liquid phosgene is likely to cause severe skin burns and eye irritation. Pulmonary edema, bronchiolitis,

and emphysema were found in cats and guinea pigs exposed to 2.5–6.25 ppm of phosgene/day for 2–41 days. A variety of animals exposed to 0.2 or 1.1 ppm for 5 hours per day for 5 days also had pulmonary edema. The TLV (threshold limit value) and the OSHA PEL (permissible exposure limit) for phosgene are 0.1 ppm (0.4 mg/m³) as an 8-hour time-weighted average. NIOSH has recommended a limit of 0.2 ppm over any 15-min period.

Laboratory operations involving phosgene require the use of the general procedures outlined in Part VI-C. Work with phosgene should always be carried out within a hood. Unused quantities of phosgene greater than 1 g should be destroyed by reaction with water or dilute alkali. Note that for many applications phosgene can be replaced by the less hazardous reagents diphosgene and triphosgene.

(20) Sodium Cyanide (and other cyanide salts)

Inorganic cyanide salts are classified as substances with a high degree of acute toxicity. Sodium cyanide is among the fastest acting of all known poisons. The lethal oral dose for humans is 200 mg. The symptoms of cyanide overdose include weakness, headache, confusion, and, occasionally, nausea and vomiting. Higher doses may be followed by almost instantaneous death. Solutions are irritating to the skin, nose, and eyes, and cyanide is absorbed through the skin. Sodium cyanide is highly toxic to animals via the oral route: LD₅₀ (rats) = 6.4 mg/kg. It can be corrosive to the skin and the eyes, for it is highly alkaline. Sodium cyanide can also produce toxic symptoms via skin absorption and inhalation. The TLV (threshold limit value) and the OSHA PEL (permissible exposure limit) for cyanide are both 5 mg/m³ as an 8-hour time-weighted average. These limits include a warning of the potential contribution of skin absorption to the overall exposure. In 1976, NIOSH recommended that the 5-mg/m³ limit be retained but that its basis be changed from an 8-hour TWA to a 10-min ceiling.

Proper gloves should be worn when handling dry sodium cyanide. Rubber gloves and splash proof goggles should be worn when substantial amounts of sodium cyanide solution are used. Hydrolysis of sodium cyanide (and other cyanide salts) by water or acid generates HCN which is extremely hazardous. Consequently, *cyanide salts should always be handled using the general procedures outlined in Part VI-C.* All reaction equipment in which cyanides are used or produced should be placed in or over shallow pans so that spills or leaks will be contained. In the event of spills of HCN or cyanide solutions, the contaminated area should be evacuated promptly and it should be determined immediately whether anyone had been exposed to cyanide vapors or liquid splash. Consideration should be given to the need for evacuating other parts of the building or notifying other occupants that the spill has occurred. In general, it is usually best not to attempt to dilute or absorb such spills if they occur in well-ventilated areas.

Detection – Hydrogen cyanide has a characteristic odor that resembles that of bitter almonds, however, many people cannot smell it in low concentrations, and this method of detection should not be relied on. Vapor-detector tubes sensitive to 1 ppm of HCN are available commercially. The presence of free cyanide ion in aqueous solution may be detected by treating an aliquot of the sample with ferrous sulfate and an excess of sulfuric acid. A precipitate of Prussian blue indicates that free cyanide ion is present.

Storage – Sodium cyanide and acids should not be stored or transported together. An open bottle of NaCN can generate HCN in humid air, and HCN may be liberated from spills of sodium cyanide solutions.

Waste disposal – Waste solutions containing cyanides should be sealed in clearly marked bottles. Contact the Environmental Management Office to arrange disposal of these containers.

In the event of exposure – Anyone who has been exposed to HCN should be removed from the contaminated atmosphere immediately. Any contaminated clothing should be removed and the affected area deluged with water. Emergency medical attention should be obtained immediately.

Part VII. Prior Approval Requirements

A. Prior Approval Requirements for Certain PHSs

The use of certain particularly hazardous substances requires the prior approval of the Chemistry Department EHS Committee. At the time of this writing, prior approval is required for work with the compounds listed below.

Restricted Chemicals Requiring Prior Approval

<i>Arsine</i>	<i>Nickel carbonyl</i>
<i>Chlorine pentafluoride</i>	<i>Nitric oxide</i>
<i>Cyanogen chloride</i>	<i>Nitrogen trioxide</i>
<i>Diborane</i>	<i>Nitrosyl chloride</i>
<i>(not including complexes of borane such as BH₃ -THF)</i>	<i>Oxygen difluoride</i>
<i>Dimethylmercury</i>	<i>Phosphine</i>
<i>Dinitrogen tetroxide</i>	<i>Selenium hexafluoride</i>
<i>Fluorine</i>	<i>Silane</i>
<i>Germanium tetrafluoride</i>	<i>Sodium-potassium alloy</i>
<i>Hydrogen cyanide</i>	<i>Stibine</i>
<i>Hydrogen fluoride (anhydrous)</i>	<i>Sulfur tetrafluoride</i>
<i>Hydrogen selenide</i>	<i>Tellurium hexafluoride</i>

Researchers intending to work with one of these restricted chemicals must prepare a plan including a standard operating procedure for review by the EHS Committee. The proposed plan must be signed by the research supervisor who must be involved in the preparation of the plan.

The standard operating procedure should include the following components.

1. The hazards associated with the chemical should be described and details provided, as appropriate, on types of health hazards, routes of exposure, quantitative toxicity data, odor threshold, chronic toxicity, etc.
2. A step-by-step outline of the experiment or experiments that will involve the use of the restricted chemical. Details should be provided for the type of equipment that will be used and exactly how the chemical will be handled and stored.
3. Details should be provided with regard to the personal protective equipment that will be employed while handling the chemical.
4. Detailed contingency plans should be described for responding to the accidental release (e.g., spill) of the restricted chemical.
5. Procedures for the safe disposal of wastes and contaminated materials should be provided.

The plan should list the names of the researchers who will be working with the restricted substance, the exact locations of the designated area(s) in which it will be used, and the approximate amounts that will be employed in the proposed research.

Plans for work with restricted substances should be submitted for review to Scott Ide (Chemistry Department Chemical Hygiene Officer, scottide@mit.edu 324-6132, Room 18-281). Once approval has been given, any changes to the SOP should be submitted in writing to Scott Ide for review by the EHS Committee.

B. Prior Approval Requirements to Meet DHS Reporting Regulations

Researchers must obtain prior approval from the Chemistry Department EHS Coordinator before purchasing any of the 40 chemicals with low threshold reporting quantities which are a subset of the Department of Homeland Security (DHS) larger list of chemicals of interest. The Chemistry Department EHS Coordinator will inform the EHS Office when a chemical from the list is purchased (though no prior approval from the central EHS Office is required). The list of 40 chemicals with low threshold reporting can be found at this link:

https://ehs.mit.edu/site/sites/default/files/2009-02_26_COI_Short_List.pdf

Laboratories are also required to report annually on the location and quantity of any DHS chemicals present in their labs. This reporting is included as part of the Annual Chemical Reporting required to be done by a designated member of the lab (typically the EHS Representative). Reminders to complete this report are generally sent out during the month of November with the deadline near the end of January.

C. Restrictions on the Purchase of Certain Chemicals

Certain chemicals cannot be purchased without written authorization by a research supervisor; in the Chemistry Department this will normally be the faculty research advisor. At the time of this writing, this restriction applies to the chemicals listed below. For more details, see <https://vpf.mit.edu/instructions-for-purchasing-hazardous-and-dangerous-items>

Arsenic trioxide	Chlorine	Hydrogen cyanide	Nitrous oxide
Phosgene	Potassium cyanide	Sodium arsenate	Sodium cyanide

D. Prior Approval Requirements for Certain Explosive Compounds

Work with certain explosive substances may require prior approval and permission from Federal and Massachusetts regulatory agencies. Consult with Scott Ide (Chemistry Department Chemical Hygiene Officer, 324-6132, Room 18-281) well in advance of any work you are planning that will involve explosive substances.

In addition, the use of certain explosive substances also requires the prior approval of the Chemistry Department EHS Committee. At the time of this writing, prior approval is required for work with the compounds listed below.

Restricted Explosive Substances Requiring Prior Approval

- (1) Compounds with multiple N-NO₂ groups, including RDX and HMX.
- (2) Compounds with multiple O-NO₂ groups, including PETN and nitroglycerine.
- (3) Trinitrotoluene (TNT).
- (4) Urea nitrate.
- (5) Organic perchlorate (ClO₄⁻) and chlorate (ClO₃⁻) salts.

- (6) Other compounds known to be sensitive explosives.
- (7) Compounds whose structures containing a high density of functional groups such as peroxy, nitro, diazo, and azide groups may require prior approval. Consult with Scott Ide prior to beginning work with such compounds.

Researchers intending to work with one of these restricted chemicals must prepare a plan of standard operating procedures (signed by their research supervisor) for review by the EHS Committee. This plan should specify:

1. Procedures for routine handling and storage of the restricted chemical, with particular attention to limitations on the quantities of the material that can be stored and handled at one time, and requirements involving protective equipment (e.g., safety shields) and protective clothing (e.g., types of gloves and eye protection).
2. Detailed contingency plans for responding to the accidental release (e.g., spill) of the restricted substance).
3. Procedures for the safe disposal of wastes and contaminated materials.

The plan should also list the names of the researchers who will be working with the restricted substance, the exact locations of the designated area(s) in which it will be used, and the approximate amounts that will be employed in the proposed research.

Plans for work with restricted substances should be submitted for review to Scott Ide (Chemistry Department Chemical Hygiene Officer, 324-6132, Room 18-281). Once approval has been given, any changes to the plan must be submitted in writing for approval by the Chemistry Department EHS Committee.”

Part VIII. Toxic Substances Control Act (TSCA)

The Toxic Substances Control Act (TSCA) is a set of federal regulations designed to: 1) assess new chemicals for environmental and health risks before they enter the market, and 2) to remove existing chemicals from the market if they pose unreasonable risks to human and environmental health. While TSCA is primarily designed for manufacturing facilities, a subset of the TSCA regulations are applicable to research and development activities, including research at MIT. TSCA may particularly impact Department of Chemistry researchers if they transfer newly synthesized chemicals outside of their lab, or become aware of any adverse health effects associated with a newly synthesized chemical. For more information please refer to the EHS Office website. A link to MIT’s Standard Operating Procedure (SOP) regarding TSCA can be found here: <http://ehs.mit.edu/site/content/toxic-substances-control-act-tsca-procedures-core-program-compliance>

Part IX. Shipping Hazardous Materials

The shipment of hazardous materials is highly regulated. The Chemistry Department utilizes the web-based shipping management software eShipGlobal which can be accessed by this link: <https://mit.eshipglobal.com/>. You may also contact the EHS Office at 2-3477. The EHS Office offers two awareness courses: “Shipping Hazardous Chemicals Awareness” and “Shipping Biohazardous Materials Awareness”. Individuals may register for the courses at <http://ehs.mit.edu/site/training>.

Part X. Medical Surveillance

Researchers requiring advice on the health effects of chemicals involved in their work should consult the literature in the Chemistry Department Library of Laboratory Safety and should contact the Industrial Hygiene Program (452-3477, N52-496) for further assistance. Any individual who believes they may have been exposed to a hazardous substance (see Part V-A) should notify their supervisor immediately and contact the Industrial Hygiene Program. *Individuals who experience any adverse health effects from exposure to hazardous substances should immediately report to the Medical Department.* Emergency assistance can be obtained by calling extension 100. All accidents involving exposure to hazardous substances that require medical attention must be reported in writing to the laboratory supervisor and the Chemistry Department Chemical Hygiene Officer (Scott Ide, 324-6132).

Special programs of ongoing medical surveillance are available for researchers planning extended work with certain hazardous substances. Enrollment in these programs can be arranged by calling the EHS Office at 452-3477. There are no charges for these services. At this time medical surveillance programs are available for work with the following hazardous substances and classes of substances:

- asbestos
- arsenic
- beryllium
- cadmium
- carcinogens
- lead
- mercury
- thallium

It is the responsibility of the laboratory supervisor to identify workers in their group who will be engaged in research that may involve hazardous exposures requiring medical surveillance. Researchers may enroll themselves in medical surveillance programs by calling the EHS Office at 452-3477. Workers can arrange consultations with physicians concerning workplace risks, illnesses, and allergies by calling the Medical Department at 253-4904.

Part XI. Researchers with Medical Conditions

Individuals with medical conditions who are required to work with hazardous materials or processes during the course of their research may be at increased risk for injury to themselves or others. It is recommended that anyone with a pre-existing medical condition, or who develops a condition and believes that they may be at increased risk of injury because of their condition, contact MIT Occupational Medicine Services (E23-171, 3-8552) for consultation and advice on how they may safely perform their work. Supervisors who have concerns about an individual's condition and their ability to safely work in a laboratory should contact MIT Occupational Medicine Services and provide a detailed job description of his/her position.

Postdoctoral researchers in need of special accommodation as a result of a medical condition should contact the MIT Disability Services Office (E19-215, x4-0082). Students should contact MIT Office of Student Disabilities Services (7-145, x3-1674). Supervisors who have concerns regarding the individual's condition or accommodation requests should contact the appropriate Disabilities Services Office. It is MIT's policy to make every effort to provide reasonable accommodations necessary for researchers to carry out their work.

Part XII. Accidents and Emergencies

A. Organization, Responsibility, and Training

The **Emergency Action Plan Coordinator** for the Department of Chemistry is Scott Ide (324-6132). The EAP Coordinator is responsible for the Department's program with regard to the actions personnel must take in the event of fires and other emergencies. The **Fire Marshal** for the Chemistry Department is Scott Ide. The responsibilities of the Fire Marshal include coordinating the activities of the Chemistry Department Fire Wardens, and serving as liaison between department personnel and emergency responders in the event of a fire or other emergency. Every research group in the Department has a **Fire Warden**, who is generally also the Group EHS Representative (see Part II-D). The responsibilities of Fire Wardens include familiarizing members of their laboratory with emergency and evacuation procedures, carrying out monthly visual inspections of the emergency equipment in their laboratory, and conducting "sweeps" of their work area during evacuations to verify that everyone has left the building.

All Chemistry Department personnel receive training in emergency procedures as part of their initial chemical hygiene and safety training as discussed in Part III-A above. Refresher training is conducted at least once each year within each research group.

B. Emergency Procedures

1. To summon emergency police, fire, or ambulance assistance, call the Campus Police 24 hour line **100**. Report the location of the emergency, including both your building and room number. Be as specific as possible about the nature of the emergency and the type of assistance required. By clearly describing the nature of the situation, you can ensure an appropriate response. In the event of uncertainty, Campus Police are instructed to order a "full-force" response!
2. Notify other workers in the area of the nature of the emergency. If necessary, activate the fire alarm to order the evacuation of the building. **When the fire alarm sounds, all personnel, without exception, are required to leave the building.** Evacuate using the doors labeled "exit"; do not use elevators. Emergency Action Floor Plans are posted on every floor of the Department and show the location of exits, evacuation routes, and fire alarm pull stations. After evacuating the building, assemble in the designated meeting area (generally in front of the building).
3. Pre-planning to control spills and procedures for handling the accidental release of hazardous substances are discussed in Part V-C-12 of the Chemical Hygiene Plan above.
4. Part V-D of the Chemical Hygiene Plan above discusses General Procedures for Work with Flammable and Explosive Substances. This section includes a discussion of handling procedures for flammable and explosive materials (fire prevention plan), as well as procedures to follow in the event of a fire. In addition, Part IV-E includes a section on fire protection equipment.
5. If a coworker has ingested a toxic substance, have the victim drink large amounts of water (*never give anything by mouth to an unconscious person*) and obtain medical assistance at once. Attempt to learn exactly what substances were ingested and inform the medical staff as soon as possible.

6. If a coworker is bleeding severely, elevate the wound above the level of the heart and apply firm pressure directly over the wound with a clean cloth, handkerchief, or your hand. Obtain immediate medical assistance.
7. Do not touch a person in contact with a live electrical circuit – disconnect the power first!
8. In the event of fires, explosions, and releases of hazardous materials, a **Fire** or **Incident Command Post** marked with colored plastic posts and signs will be set up at the scene by the MIT emergency responders. The Chemistry Department Fire Warden and the MIT official coordinating the emergency response (“Incident Commander”) will be found at this post and personnel from the laboratory involved in the accident should contact this official to provide information and technical assistance. The Incident Commander will also serve as liaison for communicating information to the Cambridge Fire Department and MIT Campus Police. Fire Department and Police personnel will generally not follow instructions from MIT students and faculty unless authorized by the Incident Commander.

C. Laboratory Emergency Information Cards

Every laboratory door should be posted with an up-to-date green emergency information card which lists the names of all personnel working in the laboratory and information (i.e. telephone numbers) on how to reach them in the event of an emergency. It is the responsibility of laboratory supervisors (with the assistance of group EHS Representatives) to ensure that these cards are updated regularly.

D. Accident Reports

To help identify and correct unrecognized hazards, and to minimize the risk of similar accidents in the future, it is necessary that personnel prepare written reports describing the circumstances of all serious accidents. One copy of the report should be submitted to the Department EHS Coordinator (Scott Ide, scottide@mit.edu, Room 18-281, 324-6132), and one copy should be given to the supervisor of the laboratory in which the accident took place. The EHS Coordinator will forward a copy of the report to the EHS Office. Reports should be filed within one week of the date of the accident. The submitted copy should bear the original signature of the individual preparing the report and must be approved by the Research Supervisor of the lab prior to submission.

Reports must be prepared by the principal personnel involved in the accident, and should include the following.

1. The name, position, and research group of all personnel involved, and the exact location, date, and time of the accident.
2. A narrative describing what took place. If the accident involved a chemical reaction, then details of the type of reaction should be provided including a description of the type of glassware and equipment and a description of all reactants and solvents used in the experiment. Please include information about whether medical treatment is required.
3. The report should also describe what steps will be taken in the future to avoid accidents of the same type.

Written accident reports must be prepared following any of the following incidents.

1. Fires that require extinguishing or the sounding a fire alarm.
2. Any accident that results in an injury requiring medical attention.

3. Any spill of a hazardous substance that takes place outside a designated area. Any accidental release of a particularly hazardous substance requires the filing of an accident report.

Members of the Department should notify their Group EHS Representative and/or laboratory supervisor of any potentially hazardous situations or practices they are aware of in the laboratory. Safety issues involving the entire Department should be brought to the attention of the EHS Committee (see Part II-B).

In addition to the accident report above, supervisors are required to submit online the OSHA 301 Supervisor's Report of Occupational Injury/Illness to the MIT Safety Program on all injuries and illnesses, regardless of the researcher's status as a student, employee, or otherwise. OSHA regulations require that this form be submitted within twenty-four hours of an injury or illness.

A link to the report can be found through the following website: <https://adminappsts.mit.edu/injury/Entry.action?sapSystemId=PS1>.

APPENDIX I

OSHA LAB STANDARD 29 CFR 1910.1450

Occupational exposure to hazardous chemicals in laboratories-

1910.1450(a)**Scope and application.****1910.1450(a)(1)**

This section shall apply to all employers engaged in the laboratory use of hazardous chemicals as defined below.

1910.1450(a)(2)

Where this section applies, it shall supersede, for laboratories, the requirements of all other OSHA health standards in 29 CFR part 1910, subpart Z, except as follows:

1910.1450(a)(2)(i)

For any OSHA health standard, only the requirement to limit employee exposure to the specific permissible exposure limit shall apply for laboratories, unless that particular standard states otherwise or unless the conditions of paragraph (a)(2)(iii) of this section apply.

1910.1450(a)(2)(ii)

Prohibition of eye and skin contact where specified by any OSHA health standard shall be observed.

1910.1450(a)(2)(iii)

Where the action level (or in the absence of an action level, the permissible exposure limit) is routinely exceeded for an OSHA regulated substance with exposure monitoring and medical surveillance requirements paragraphs (d) and (g)(1)(ii) of this section shall apply.

1910.1450(a)(3)

This section shall not apply to:

1910.1450(a)(3)(i)

Uses of hazardous chemicals which do not meet the definition of laboratory use, and in such cases, the employer shall comply with the relevant standard in 29 CFR part 1910, subpart Z, even if such use occurs in a laboratory.

1910.1450(a)(3)(ii)

Laboratory uses of hazardous chemicals which provide no potential for employee exposure. Examples of such conditions might include:

1910.1450(a)(3)(ii)(A)

Procedures using chemically-impregnated test media such as Dip-and-Read tests where a reagent strip is dipped into the specimen to be tested and the results are interpreted by comparing the color reaction to a color chart supplied by the manufacturer of the test strip; and

1910.1450(a)(3)(ii)(B)

Commercially prepared kits such as those used in performing pregnancy tests in which all of the reagents needed to conduct the test are contained in the kit.

1910.1450(b)**Definitions —**

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

Assistant Secretary means the Assistant Secretary of Labor for Occupational Safety and Health, U.S. Department of Labor, or designee.

Carcinogen (see select carcinogen).

Chemical Hygiene Officer means an employee who is designated by the employer, and who is qualified by training or experience, to provide technical guidance in the development and implementation of the provisions of the Chemical Hygiene Plan. This definition is not intended to place limitations on the position description or job classification that the designated individual shall hold within the employer's organizational structure.

Chemical Hygiene Plan means a written program developed and implemented by the employer which sets forth procedures, equipment, personal protective equipment and work practices that (i) are capable of protecting employees from the health hazards presented by hazardous chemicals used in that particular workplace and (ii) meets the requirements of paragraph (e) of this section.

Combustible liquid means any liquid having a flashpoint at or above 100 deg. F (37.8 deg. C), but below 200 deg. F (93.3 deg. C), except any mixture having components with flashpoints of 200 deg. F (93.3 deg. C), or higher, the total volume of which make up 99 percent or more of the total volume of the mixture.

Compressed gas means:

- (i) A gas or mixture of gases having, in a container, an absolute pressure exceeding 40 psi at 70 deg. F (21.1 deg. C); or
- (ii) A gas or mixture of gases having, in a container, an absolute pressure exceeding 104 psi at 130 deg. F (54.4 deg. C) regardless of the pressure at 70 deg. F (21.1 deg. C); or
- (iii) A liquid having a vapor pressure exceeding 40 psi at 100 deg. F (37.8 C) as determined by ASTM D-323-72.

Designated area means an area which may be used for work with "select carcinogens," reproductive toxins or substances which have a high degree of acute toxicity. A designated area may be the entire laboratory, an area of a laboratory or a device such as a laboratory hood.

Emergency means any occurrence such as, but not limited to, equipment failure, rupture of containers or failure of control equipment which results in an uncontrolled release of a hazardous chemical into the workplace.

Employee means an individual employed in a laboratory workplace who may be exposed to hazardous chemicals in the course of his or her assignments.

Explosive means a chemical that causes a sudden, almost instantaneous release of pressure, gas, and heat when subjected to sudden shock, pressure, or high temperature.

Flammable means a chemical that falls into one of the following categories:

- (i) **Aerosol, flammable** means an aerosol that, when tested by the method described in 16 CFR 1500.45, yields a flame protection exceeding 18 inches at full valve opening, or a flashback (a flame extending back to the valve) at any degree of valve opening;
- (ii) **Gas, flammable** means:
 - (A) A gas that, at ambient temperature and pressure, forms a flammable mixture with air at a concentration of 13 percent by volume or less; or
 - (B) A gas that, at ambient temperature and pressure, forms a range of flammable mixtures with air wider than 12 percent by volume, regardless of the lower limit.
- (iii) **Liquid, flammable** means any liquid having a flashpoint below 100 deg F (37.8 deg. C), except any mixture having components with flashpoints of 100 deg. C) or higher, the total of which make up 99 percent or more of the total volume of the mixture.
- (iv) **Solid, flammable** means a solid, other than a blasting agent or explosive as defined in § 1910.109(a), that is liable to cause fire through friction, absorption of moisture, spontaneous chemical change, or retained heat from manufacturing or processing, or which can be ignited readily and when ignited burns so vigorously and persistently as to create a serious hazard. A chemical shall be considered to be a flammable solid if, when tested by the method described in 16 CFR 1500.44, it ignites and burns with a self-sustained flame at a rate greater than one-tenth of an inch per second along its major axis.

Flashpoint means the minimum temperature at which a liquid gives off a vapor in sufficient concentration to ignite when tested as follows:

- (i) Tagliabue Closed Tester (See American National Standard Method of Test for Flash Point by Tag Closed Tester, Z11.24 - 1979 (ASTM D 56-79)) - for liquids with a viscosity of less than 45 Saybolt Universal Seconds (SUS) at 100 deg. F (37.8 deg. C), that do not contain suspended solids and do not have a tendency to form a surface film under test; or
- (ii) Pensky-Martens Closed Tester (See American National Standard Method of Test for Flashpoint by Pensky-Martens Closed Tester, Z11.7 - 1979 (ASTM D 93-79)) - for liquids with a viscosity equal to or greater than 45 SUS at 100 deg. F (37.8 deg. C), or that contain suspended solids, or that have a tendency to form a surface film under test; or
- (iii) Setaflash Closed Tester (see American National Standard Method of test for Flash Point by Setaflash Closed Tester (ASTM D 3278-78)).

Organic peroxides, which undergo autoaccelerating thermal decomposition, are excluded from any of the flashpoint determination methods specified above.

Hazardous chemical means a chemical for which there is statistically significant evidence based on at least one study conducted in accordance with established scientific principles that acute or chronic health effects may occur in exposed employees. The term “health hazard” includes chemicals which are carcinogens, toxic or highly toxic agents, reproductive toxins, irritants, corrosives, sensitizers, hepatotoxins, nephrotoxins, neurotoxins, agents which act on the hematopoietic systems, and agents which damage the lungs, skin, eyes, or mucous membranes.

Appendices A and B of the Hazard Communication Standard (29 CFR 1910.1200) provide further guidance in defining the scope of health hazards and determining whether or not a chemical is to be considered hazardous for purposes of this standard.

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

Laboratory scale means 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. “Laboratory scale” excludes those workplaces whose function is to produce commercial quantities of materials.

Laboratory-type hood means a device located in a laboratory, enclosure on five sides with a movable sash or fixed partial enclosed on the remaining side; constructed and maintained to draw air from the laboratory and to prevent or minimize the escape of air contaminants into the laboratory; and allows chemical manipulations to be conducted in the enclosure without insertion of any portion of the employee’s body other than hands and arms.

Walk-in hoods with adjustable sashes meet the above definition provided that the sashes are adjusted during use so that the airflow and the exhaust of air contaminants are not compromised and employees do not work inside the enclosure during the release of airborne hazardous chemicals.

Laboratory use of hazardous chemicals means handling or use of such chemicals in which all of 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.

Medical consultation means a consultation which takes place between an employee and a licensed physician for the purpose of determining what medical examinations or procedures, if any, are appropriate in cases where a significant exposure to a hazardous chemical may have taken place.

Organic peroxide means an organic compound that contains the bivalent -O-O- structure and which may be considered to be a structural derivative of hydrogen peroxide where one or both of the hydrogen atoms has been replaced by an organic radical.

Oxidizer means a chemical other than a blasting agent or explosive as defined in § 1910.109(a), that initiates or promotes combustion in other materials, thereby causing fire either of itself or through the release of oxygen or other gases.

Physical hazard means 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.

Protective laboratory practices and equipment means those laboratory procedures, practices and equipment accepted by laboratory health and safety experts as effective, or that the employer can show to be effective, in minimizing the potential for employee exposure to hazardous chemicals.

Reproductive toxins means chemicals which affect the reproductive capabilities which affect the reproductive capabilities including chromosomal damage (mutations) and effects on fetuses (teratogenesis).

Select carcinogen means any substance which meets one of the following criteria:

- (i) It is regulated by OSHA as a carcinogen; or
- (ii) It is listed under the category, “known to be carcinogens,” in the Annual Report on Carcinogens published by the National Toxicology Program (NTP)(latest edition); or
- (iii) It is listed under Group 1 (“carcinogenic to humans”) by the International Agency for research on Cancer Monographs (IARC)(latest editions); or

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

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

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

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

Unstable (reactive) means a chemical which is the pure state, or as produced or transported, will vigorously polymerize, decompose, condense, or will become self-reactive under conditions of shocks, pressure or temperature.

Water-reactive means a chemical that reacts with water to release a gas that is either flammable or presents a health hazard.

1910.1450(c)

Permissible exposure limits. For laboratory uses of OSHA regulated substances, the employer shall assure that laboratory employees’ exposures to such substances do not exceed the permissible exposure limits specified in 29 CFR part 1910, subpart Z.

1910.1450(d)

Employee exposure determination —

1910.1450(d)(1)

Initial monitoring. The employer shall measure the employee’s exposure to any substance regulated by a standard which requires monitoring if there is reason to believe that exposure levels for that substance routinely exceed the action level (or in the absence of an action level, the PEL).

1910.1450(d)(2)

Periodic monitoring. If the initial monitoring prescribed by paragraph (d)(1) of this section discloses employee exposure over the action level (or in the absence of an action level, the PEL), the employer shall immediately comply with the exposure monitoring provisions of the relevant standard.

1910.1450(d)(3)

Termination of monitoring. Monitoring may be terminated in accordance with the relevant standard.

1910.1450(d)(4)

Employee notification of monitoring results. The employer shall, within 15 working days after the receipt of any monitoring results, notify the employee of these results in writing either individually or by posting results in an appropriate location that is accessible to employees.

1910.1450(e)

Chemical hygiene plan — General. (Appendix A of this section is non-mandatory but provides guidance to assist employers in the development of the Chemical Hygiene Plan).

1910.1450(e)(1)

Where hazardous chemicals as defined by this standard are used in the workplace, the employer shall develop and carry out the provisions of a written Chemical Hygiene Plan which is:

1910.1450(e)(1)(i)

Capable of protecting employees from health hazards associated with hazardous chemicals in that laboratory and

1910.1450(e)(1)(ii)

Capable of keeping exposures below the limits specified in paragraph (c) of this section.

1910.1450(e)(2)

The Chemical Hygiene Plan shall be readily available to employees, employee representatives and, upon request, to the Assistant Secretary.

1910.1450(e)(3)

The Chemical Hygiene Plan shall include each of the following elements and shall indicate specific measures that the employer will take to ensure laboratory employee protection;

1910.1450(e)(3)(i)

Standard operating procedures relevant to safety and health considerations to be followed when laboratory work involves the use of hazardous chemicals;

1910.1450(e)(3)(ii)

Criteria that the employer will use to determine and implement control measures to reduce employee exposure to hazardous chemicals including engineering controls, the use of personal protective equipment and hygiene practices; particular

attention shall be given to the selection of control measures for chemicals that are known to be extremely hazardous;

1910.1450(e)(3)(iii)

A requirement that fume hoods and other protective equipment are functioning properly and specific measures that shall be taken to ensure proper and adequate performance of such equipment;

1910.1450(e)(3)(iv)

Provisions for employee information and training as prescribed in paragraph (f) of this section;

1910.1450(e)(3)(v)

The circumstances under which a particular laboratory operation, procedure or activity shall require prior approval from the employer or the employer's designee before implementation;

1910.1450(e)(3)(vi)

Provisions for medical consultation and medical examinations in accordance with paragraph (g) of this section;

1910.1450(e)(3)(vii)

Designation of personnel responsible for implementation of the Chemical Hygiene Plan including the assignment of a Chemical Hygiene Officer, and, if appropriate, establishment of a Chemical Hygiene Committee; and

1910.1450(e)(3)(viii)

Provisions for additional employee protection for work with particularly hazardous substances. These include "select carcinogens," reproductive toxins and substances which have a high degree of acute toxicity. Specific consideration shall be given to the following provisions which shall be included where appropriate:

1910.1450(e)(3)(viii)(A)

Establishment of a designated area;

1910.1450(e)(3)(viii)(B)

Use of containment devices such as fume hoods or glove boxes;

1910.1450(e)(3)(viii)(C)

Procedures for safe removal of contaminated waste; and

1910.1450(e)(3)(viii)(D)

Decontamination procedures.

1910.1450(e)(4)

The employer shall review and evaluate the effectiveness of the Chemical Hygiene Plan at least annually and update it as necessary.

1910.1450(f)

Employee information and training.

1910.1450(f)(1)

The employer shall provide employees with information and training to ensure that they are apprised of the hazards of chemicals present in their work area.

1910.1450(f)(2)

Such information shall be provided at the time of an employee's initial assignment to a work area where hazardous chemicals are present and prior to assignments involving new exposure situations. The frequency of refresher information and training shall be determined by the employer.

1910.1450(f)(3)

Information. Employees shall be informed of:

1910.1450(f)(3)(i)

The contents of this standard and its appendices which shall be made available to employees;

1910.1450(f)(3)(ii)

the location and availability of the employer's Chemical Hygiene Plan

1910.1450(f)(3)(iii)

The permissible exposure limits for OSHA regulated substances or recommended exposure limits for other hazardous chemicals where there is no applicable OSHA standard;

1910.1450(f)(3)(iv)

Signs and symptoms associated with exposures to hazardous chemicals used in the laboratory; and

1910.1450(f)(3)(v)

The location and availability of known reference material on the hazards, safe handling, storage and disposal of hazardous chemicals found in the laboratory including, but not limited to, Material Safety Data Sheets received from the chemical supplier.

1910.1450(f)(4)

Training.

1910.1450(f)(4)(i)

Employee training shall include:

1910.1450(f)(4)(i)(A)

Methods and observations that may be used to detect the presence or release of a hazardous chemical (such as monitoring conducted by the employer, continuous monitoring devices, visual appearance or odor of hazardous chemicals when being released, etc.);

1910.1450(f)(4)(i)(B)

The physical and health hazards of chemicals in the work area; and

1910.1450(f)(4)(i)(C)

The measures employees can take to protect themselves from these hazards, including specific procedures the employer has implemented to protect employees from exposure to hazardous chemicals, such as appropriate work practices, emergency procedures, and personal protective equipment to be used.

1910.1450(f)(4)(ii)

The employee shall be trained on the applicable details of the employer's written Chemical Hygiene Plan.

1910.1450(g)

Medical consultation and medical examinations.

1910.1450(g)(1)

The employer shall provide all employees who work with hazardous chemicals an opportunity to receive medical attention, including any follow-up examinations which the examining physician determines to be necessary, under the following circumstances:

1910.1450(g)(1)(i)

Whenever an employee develops signs or symptoms associated with a hazardous chemical to which the employee may have been exposed in the laboratory, the employee shall be provided an opportunity to receive an appropriate medical examination.

1910.1450(g)(1)(ii)

Where exposure monitoring reveals an exposure level routinely above the action level (or in the absence of an action level, the PEL) for an OSHA regulated substance for which there are exposure monitoring and medical surveillance requirements, medical surveillance shall be established for the affected employee as prescribed by the particular standard.

1910.1450(g)(1)(iii)

Whenever an event takes place in the work area such as a spill, leak, explosion or other occurrence resulting in the likelihood of a hazardous exposure, the affected employee shall be provided an opportunity for a medical consultation. Such consultation shall be for the purpose of determining the need for a medical examination.

1910.1450(g)(2)

All medical examinations and consultations shall be performed by or under the direct supervision of a licensed physician and shall be provided without cost to the employee, without loss of pay and at a reasonable time and place.

1910.1450(g)(3)

Information provided to the physician. The employer shall provide the following information to the physician:

1910.1450(g)(3)(i)

The identity of the hazardous chemical(s) to which the employee may have been exposed;

1910.1450(g)(3)(ii)

A description of the conditions under which the exposure occurred including quantitative exposure data, if available; and

1910.1450(g)(3)(iii)

A description of the signs and symptoms of exposure that the employee is experiencing, if any.

1910.1450(g)(4)

Physician's written opinion.

1910.1450(g)(4)(i)

For examination or consultation required under this standard, the employer shall obtain a written opinion from the examining physician which shall include the following:

1910.1450(g)(4)(i)(A)

Any recommendation for further medical follow-up;

1910.1450(g)(4)(i)(B)

The results of the medical examination and any associated tests;

1910.1450(g)(4)(i)(C)

Any medical condition which may be revealed in the course of the examination which may place the employee at increased risk as a result of exposure to a hazardous workplace; and

1910.1450(g)(4)(i)(D)

A statement that the employee has been informed by the physician of the results of the consultation or medical examination and any medical condition that may require further examination or treatment.

1910.1450(g)(4)(ii)

The written opinion shall not reveal specific findings of diagnoses unrelated to occupational exposure.

1910.1450(h)**Hazard identification.****1910.1450(h)(1)**

With respect to labels and material safety data sheets:

1910.1450(h)(1)(i)

Employers shall ensure that labels on incoming containers of hazardous chemicals are not removed or defaced.

1910.1450(h)(1)(ii)

Employers shall maintain any material safety data sheets that are received with incoming shipments of hazardous chemicals, and ensure that they are readily accessible to laboratory employees.

1910.1450(h)(2)

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

1910.1450(h)(2)(i)

If the composition of the chemical substance which is produced exclusively for the laboratory's use is known, the employer shall determine if it is a hazardous chemical as defined in paragraph (b) of this section. If the chemical is determined to be hazardous, the employer shall provide appropriate training as required under paragraph (f) of this section.

1910.1450(h)(2)(ii)

If the chemical produced is a byproduct whose composition is not known, the employer shall assume that the substance is hazardous and shall implement paragraph (e) of this section.

1910.1450(h)(2)(iii)

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

1910.1450(i)

Use of respirators. Where the use of respirators is necessary to maintain exposure below permissible exposure limits, the employer shall provide, at no cost to the employee, the proper respiratory equipment. Respirators shall be selected and used in accordance with the requirements of 29 CFR 1910.134.

1910.1450(j)**Recordkeeping.****1910.1450(j)(1)**

The employer shall establish and maintain for each employee an accurate record of any measurements taken to monitor employee exposures and any medical consultation and examinations including tests or written opinions required by this standard.

1910.1450(j)(2)

The employer shall assure that such records are kept, transferred, and made available in accordance with 29 CFR 1910.1020.

1910.1450(k)**Dates —****1910.1450(k)(1)**

Effective date. This section shall become effective May 1, 1990.

1910.1450(k)(2)

Start-up dates.

1910.1450(k)(2)(i)

Employers shall have developed and implemented a written Chemical Hygiene Plan no later than January 31, 1991.

1910.1450(k)(2)(ii)

Paragraph (a)(2) of this section shall not take effect until the employer has developed and implemented a written Chemical Hygiene Plan.

APPENDIX II

Chemical Hygiene Quiz Questions

- (1) Where is your personal copy of the Chemical Hygiene Plan? Demonstrate your familiarity with it by describing how it's organized and outlining its major sections.
- (2) Where can you find a copy of the OSHA Lab Standard?
- (3) Who is the EH&S Representative for your research group? What are his/her responsibilities?
- (4) Where is the Chemistry Department Library of Lab Safety? What's in it? What safety and chemical hygiene books are available in your research group library?
- (5) What is an SDS? SDS's are on file at MIT for all compounds purchased. Where would you go to obtain an SDS for the compounds you are using?
- (6) Make a list of the ten reagents and solvents you used recently (refresher review question). For each, describe what you know about its acute toxicity and hazards as a carcinogen and reproductive toxin.
- (7) According to the OSHA Lab Standard, what distinguishes a "particularly hazardous substance" from other hazardous chemicals?
- (8) Each research group is required to maintain certain inventory lists of hazardous substances. Where is your research group's inventory of hazardous chemicals? Where is your group's list of "particularly hazardous substances"?
- (9) What special measures and precautions are associated with particularly hazardous substances?
- (10) What is a designated area? What can and cannot be done in such an area?
- (11) For people working at lab hoods equipped with Phoenix Fume Hood Monitors: what does it mean when the red caution light goes on? What action should you take?
- (12) What are the training requirements for fire extinguisher usage? List all of the types of fire extinguishers available in your lab. Where is the nearest fire extinguisher to your lab bench? What type of extinguisher is it? What type of extinguisher is most suitable for a wastebasket paper trash fire? On an ether spill fire? A fire involving potassium metal or LAH? Electrical equipment fire?
- (13) Describe the procedures you use with regard to wearing gloves: do you always wear gloves? Do you ever wear two pairs? When? Do you always remove them before handling things like pens, telephones, doorknobs, etc.?
- (14) What rules govern solvent storage?

- (15) What are the rules governing working alone in the lab or at night?
- (16) What substances (if any) can be disposed of down the drain?
- (17) How do you dispose of waste mercury? Sodium? LiAlH_4 ?
- (18) What rules govern the purchase of chemicals in “lecture bottles”?
- (19) Consider the reactions you’ve run the last day or so, and the chemicals involved in each: describe exactly what you would have done in the event that the container holding each substance had broken and spilled its contents on the floor of your lab? What if the reaction flask had broken releasing its contents? (Refresher review questions)
- (20) Describe exactly what you would do in each case if your body and clothes were splashed with the various chemicals and mixtures you’ve worked with during the past several days. (Refresher review)
- (21) Does your group have a spill control kit? Where is it? What’s in it?
- (22) What action would you take if a pint of diethyl ether spilled on the floor of your laboratory? How about a spill of concentrated sulfuric acid? Bromine?
- (23) What common solvents and compounds form peroxides? How do you test a sample for the presence of peroxides? What do you do if a solvent tests positive?
- (24) What would you do if your labmate’s clothes were on fire?
- (25) What is the flame resistant lab coat policy in our Department? What kind of flame resistant lab coat is required when working with tert-butyllithium inside of a fume hood? Are there areas of the lab that are exempt from the policy? If so, under what conditions was the exemption made?
- (26) What hazards are associated with using liquid nitrogen-cooled vacuum traps? What precautions should you take?
- (27) When must an accident report be filed? What does it consist of? Who does it go to?

Section Two: Working with Biological Hazards

A. Introduction

Biological hazards are agents of biological origin that present a possible threat to the environment or to the health of laboratory personnel. Such materials include, but are not limited to, cells, viruses, spent media used for their propagation, animal or human tissues, genetic material of pathogenic organisms and any nucleic acid that is categorized as “recombinant DNA.”

This document provides an overview of the procedures to be used while working with biological hazards in the Department. It is not meant to be a detailed safety manual because such documents are available through the **Biosafety Program** and other units within the Institute. Rather, the following is a resource identification guide to the more comprehensive safety documents published by groups within MIT charged with protection against exposure to specific biohazardous agents.

Services relating to the physical methods of biohazard control at MIT are provided by four offices:

Industrial Hygiene Program	N52-496, 452-3477
Radiation Protection Program	N52-496, 452-3477
Biosafety Program	N52-496, 452-3477
Division of Comparative Medicine	253-1756

In the discussion below, reference will be made to six documents which are available to every laboratory through the EHS Office (documents 1 and 2), the MIT Division of Comparative Medicine (DCM; documents 3-5), and the Biological Engineering Division of Toxicology (document 6). These six documents are part of the collection of safety literature in the Department Library of Lab Safety.

Resource documents:

1. MIT Biosafety Manual
2. Required Procedures for Radiation Protection
3. Laboratory Animal User's Handbook
4. MIT Toxicology Safety Manual

B. Registration of Personnel Working with Biohazardous Materials

It is the responsibility of the Principal Investigator (usually a faculty member) to register with EHS Office and (if necessary) DCM prior to working with materials classified as biohazardous. The specific registration procedures typically require a written application. Since the procedures vary greatly with the nature of the work being conducted, it is best to contact EHS or DCM directly to obtain the appropriate registration forms. For some proposed work, detailed review by an Institute Committee (Committee on Assessment of Biohazards, Committee on Animal Care, etc.) must precede formal authorization. Registration procedures for projects involving recombinant DNA research and other work formally defined as “biohazardous” are online at <http://ehs.mit.edu/site/content/biological-research-registration>. Procedures for work with animals in which a risk is posed to the investigator are in the Lab Animal User's Handbook [section XI, Occupational Health].

Examples of specific procedures involving work with biological hazards and the corresponding office within MIT through which authorization must be sought are given in the next section.

C. Biohazard Classification

(a) Projects that must be registered with the Committee on Assessment of Biohazards.

1. **All** recombinant DNA projects, including studies considered *exempt* under the NIH guidelines.
2. **All** studies with human source material (e.g., blood, serum, cells, etc.) Such materials pose hazards from potentially pathogenic agents, hepatitis virus, human T-cell leukemia virus (HTLV), and human immunodeficiency virus (HIV). Personnel working with potentially infectious material must attend an OSHA-mandated training session (see Section D).

The contact office within MIT is the Biosafety Program (x 2-3477).

(b) Projects that must be registered with the Committee on Animal Care.

All projects involving live animals require the authorization of the Committee on Animal Care. An example of a project needing this authorization would be one in which pathogenic viruses are to be isolated from the tissues of experimental animals. This project would require the authorization of the Committee on Animal Care (contact the DCM), as well as the approval of the Committee on Assessment of Biohazards (contact the Biosafety Program).

(c) Projects that must be registered with the Committee on the Use of Humans as Experimental Subjects.

An example of such a study would be one in which enzymes are isolated from a human tissue, such as placenta. Owing to the significant incidence of transmissible diseases in the population, all human tissues should be considered as having infectious potential. The office to contact is that of Judith Medeiros-Adams (x 3-6787).

(d) Projects that must be registered with the Radiation Protection Program.

Note that **all** projects involving radioactive substances require the authorization of the RPP, regardless of whether or not a biohazard is generated. There are many experiments in which a radioactive biohazardous agent is generated (e.g., a radioactive AIDS virus or a pathogenic bacterial cell). The use *and disposal* of these agents requires special procedures, and investigators are required to contact the RPP for guidelines prior to the start of the experiment [see resource document 2 (p. 20) and contact the RPP at x 2-3477].

D. Procedures for Personnel Working with Potentially Pathogenic Agents

“Bloodborne Pathogens” refers to microorganisms potentially present in human blood that can cause human diseases. Examples are Hepatitis B Virus (HBV) and HIV. OSHA defines potentially infectious materials containing such pathogens as including human blood components, products made from human blood, various body fluids, and HIV or HBV containing cell or tissue cultures and media.

All personnel carrying out studies that involve possible occupational exposure to bloodborne pathogens must, before beginning any work, complete *Bloodborne Pathogen Training*. All members of groups involved in such studies must participate annually in a group (OSHA-mandated) training

program on bloodborne pathogens held by the Biosafety Program that is specifically designed around the individual laboratory's work and needs. In addition, it is strongly recommended that all such personnel working with human blood, body fluids and tissues receive a recombinant DNA vaccine which is available for HBV. This vaccine is offered by EHS Office free of charge. A vaccination acceptance/declination form is provided during Bloodborne Pathogens Training or upon request from the Biosafety Office (x 2-3477).

E. Containment of Biohazardous Material

Containment is the minimization of risk to personnel and the environment from biohazardous material. There are two levels of containment.

Primary containment includes safety techniques and devices used to separate personnel physically from the biohazard. Specific examples include the use of protective laboratory clothing, the use of aseptic technique in a manner that avoids environmental spread of the pathogenic agent in use, and the use of biosafety cabinets to minimize the spread of aerosols.

Secondary containment pertains to laboratory design and operational features used to protect the environment by physically containing the biohazardous agent within the laboratory. Specific examples of secondary containment considerations are the use of non-porous surfaces for benchtops and floors in the laboratory, the type of door used to separate the laboratory from public areas, the type of ventilation system in use, and the location of autoclaves proximal to the site of biohazard research. The key resource documents dealing with containment are those of the Division of Toxicology [document 6, section entitled "Biohazards"] and the NIH recombinant DNA Research Guidelines http://oba.od.nih.gov/rdna/nih_guidelines_oba.html.

The required level of primary or secondary containment is in direct relation to the perceived risk of the biohazardous agent being used. Four levels of physical confinement (**BIOSAFETY-LEVELS**, BL-1 through BL-4) are defined by local, national or Institute codes [see resource documents 1 (section on "Containment") and 6 (section on "Biohazards")] and are as follows:

- BL-1.** Minimal or no hazard to personnel or the environment. Most work at MIT falls into this category. Note that all recombinant DNA research is at least BL-1.
- BL-2.** Potentially pathogenic organisms are used; this includes plant or animal pathogens and all human materials (including cell lines).
- BL-2+.** Work with agents known to cause serious disease. BL-3 protocols are followed but in a designated normal laboratory with closed doors. All equipment for experimental work is located in that laboratory.
- BL-3.** Threat of serious or lethal disease. Typical examples include work with high titers of HIV. A specialized laboratory with key-card entry is mandated. MIT does not have any labs suitable for BL-3 research at this time.
- BL-4.** Extremely hazardous infectious agents. BL-4 work is neither authorized nor planned at MIT owing in part to local codes, and will not be considered further here.

F. Storage, Decontamination, and Disposal of Biohazardous Material

Specific procedures for storage, decontamination and disposal of biohazardous agents have been formulated by the Biosafety Office. Information on decontamination and disposal is available at <http://ehs.mit.edu/site/content/biologically-contaminated-waste>

(1) Storage and growth of living biohazardous agents.

BIOHAZARD labels, available from the Biosafety Program (2-3477), must be affixed to any equipment used to store (e.g., refrigerators), grow (e.g., incubators), or manipulate (e.g., centrifuges) biohazardous agents.

(2) Storage of needle and syringes.

Laboratory and animal facility stores of needles and syringes should be kept secured at all times either in a locked laboratory cabinet or in a locked laboratory space. All needles and syringes, regardless of their use, must be placed in designated sharps containers for disposal. Even needles and or syringes that are not used for injection of materials into animals but are part of laboratory created equipment or set-up must be placed in designated sharps containers for disposal. The intent of this policy is to prevent accidental injuries and theft.

(3) Storage of biohazardous waste.

1. **BL-1 and BL-2 Solid waste.** Solid waste containers shall consist of a terminal (nonreusable) biohazard bag in a labeled, covered, leak-proof container located in an appropriately marked and confined area.
2. **BL-1 and BL-2 Liquid waste.** BL-1 waste may be stored in a covered container in the laboratory prior to chemical decontamination. BL-2 waste, by contrast, must be chemically decontaminated immediately after its generation.
3. **Sharps waste.** Physically hazardous waste (e.g., sharps) which is biologically contaminated must be collected in a sharps bin for removal by trained EHS technicians.

(4) Treatment of biohazardous waste.

Organisms may be rendered innocuous by chemical disinfection (e.g., by bleach or Wescodyne) or wet heat sterilization (autoclaving). Detailed procedures customized to specific experimental protocols are outlined in the lab's biological research registration.

There recently has been a change in state regulation [105 CMR 480.000] requiring MIT and other institutions to document the storage and disposal of medical and biological waste. It is now necessary for all autoclave facilities to completely fill out the MIT waste log book for all waste treatment autoclave cycles. To verify the sterilization effectiveness of the autoclave, biological spore tests must be performed monthly. Details of this autoclave validation test are available online at <https://ehs.mit.edu/site/content/autoclave-validation-program>.

As part of the waste treatment process, a tag is affixed to the biohazardous waste. This tag has on it the specific identification number of the Principal Investigator (the faculty member in charge of the research). Note that this tag stays with the bag permanently. Tags are available from the Biosafety Program.

(5) Disposal of non-infectious biological waste.

1. **Solid waste.** There are two types of decontaminated solid waste: autoclaved solids and chemically treated solids. Once these materials have been rendered noninfectious, all BIOHAZARD signs or symbols must be removed from sight. The formerly biohazardous waste is then removed by the custodian. Note that the all sharps are incinerated off-site and NO sharps are removed by the custodians.
2. **Liquid waste.** Once liquid waste such as spent bacteriological media has been rendered non-infectious by chemical treatment, it can be disposed of by washing down the sink.

(6) Treatment and disposal of radioactive biohazardous waste.

Wherever possible, radioactive biohazardous waste should be treated chemically to render it non-infectious. It should then be disposed of as radioactive waste by the Radiation Protection Program. It is noted that such disposal procedures must be approved by the RPP prior to doing the experiment [see resource document 2, p. 20].

G. Medical Surveillance

The Institute offers a voluntary health screening program for personnel doing recombinant DNA research. The tests are provided at no cost to the individual. The program involves a periodic health history plus selected laboratory tests. Follow-up testing involves repeated laboratory tests at yearly intervals. Any medical abnormalities that may be revealed are investigated further to determine the probable cause. Although there is no known harm linked to occupational exposure at MIT to recombinant DNA materials, the Institute wishes to be alert to possible consequences of exposure to these agents. To enroll in this program, contact Claudia Mickelson of the Biosafety Program at x2-3477.

H. Accidents

Much of the information above was aimed at preventing the accidental exposure of personnel or the environment to biohazardous materials. Even with careful laboratory practice, however, accidents will happen and there are specific procedures that must be followed for clean-up, post-accident medical treatment of exposed researchers, and reporting.

(1) Spills

Spills that have occurred inside a hood are the easiest to render innocuous provided the clean-up procedures are initiated while the cabinet continues to operate effectively. The procedures typically involve spraying or flooding the work area with a disinfectant solution and then autoclaving the clean-up materials, including work gloves and paper towels.

Spills of BL2 or BL2+ materials occurring outside a safety cabinet may require more extreme measures. These include warning other personnel in the laboratory and quickly leaving the room while holding your breath. Before reentering the laboratory, you must wait at least 30 minutes to allow aerosols to settle. Contaminated garments must be removed and autoclaved. Prior to initiating the decontamination process, you must put on clean protective clothing and, with extremely pathogenic agents, you must wear a respirator. Further details concerning the clean-up of such spills can be found in document 1.

When the spilled biohazardous material is also radioactive, the Radiation Protection Program must be notified immediately (x 2-3477). A representative of the RPP will survey the spill to determine

the extent of additional risk due to the radionuclide in use. It is likely that the RPP officer will determine that decontamination **cannot** be accomplished by autoclaving. In this event, an option must be available for chemical decontamination (see resource document 1).

(2) Accidental exposure of personnel

People are exposed to biohazardous agents by four routes. These include ingestion (for example, by mouth pipetting — **which is a violation of MIT safety procedures** — inhalation of aerosols, absorption of biohazardous material through membranes or through cuts in membranes, and accidental inoculation by needles or other sharp objects.

Any exposure of the eyes to a biohazard should be treated immediately by flushing with water from an eye wash. Exposure of skin to a biohazard should be treated by showering with water or, in selected cases, by alcohol wipes. Seek medical attention immediately if necessary. Examples of when this is necessary include a needlestick, or splash to the face with blood or body fluids.

Workers exposed to biohazardous agents should immediately report the incident to the Principal Investigator responsible for the research project. The Principal Investigator should use his or her judgment in determining the need to report the accident to the Biosafety Program (x 2-3477). Additional examples of accidents that need to be reported and those that do not are given in document 1 [section on “Accidents”].

The Principal Investigator must be knowledgeable of the risks associated with the specific organisms with which he or she is working and should have **in place** an emergency plan that identifies specific medical personnel who should be consulted in the event of accidental exposure of research workers.

Section Three: Working with Electrical Hazards

A. Introduction

There are inherent dangers involved when using any electrical equipment and therefore care must be exercised when operating and especially when installing, modifying, and/or repairing any electrical equipment. Electrical shock – the passage of current through the human body – is the major electrical hazard. The diverse types of electrical equipment used in the chemistry department includes lasers, power supplies, electrophoresis apparatus, electrochemical set ups, X-ray equipment, hot plates and heating mantles. Work involving any of these various classes of equipment can lead to serious injuries if prudent electrical practices are not followed. In order to assure the safe operation of electrical equipment, all electrical equipment must be installed and maintained in accordance with the provisions of the National Electric Code (NEC) of the National Fire Protection Agency.

Modifications and repairs to the receptacle and wiring in the walls is the responsibility of Physical Plant and should not be attempted or carried out by anyone else. Also, it is strongly advised that all work on electrical equipment be carried out by qualified personnel. Before attempting any minor repairs, modifications, or installations of electrical equipment it is advised that the MIT Accident Prevention Guide #3 dealing with electrical safety and practices be consulted, as well as the NEC handbook section on electrical safety. Copies of these books can be found in the Chemistry Department Library of Lab Safety located in Building 18 on the second floor next to the copy machine. Also, before carrying out any minor repairs, modifications, or installations of electrical equipment, it is required that the equipment be deenergized and all capacitors safely discharged. Furthermore, this deenergized and/or discharged condition must be verified before proceeding. It is

suggested that you consult with MIT's Electrical Services, part of physical plant, before attempting any repairs, modifications or installations of electrical equipment.

(1) Proper Wiring

The installation, replacement, modification, repair or rehabilitation of any part of any electrical installation must be in compliance with NEC standards, which specify the proper wiring. For any piece of electrical equipment, there must be a switch in a convenient and readily accessible location that will disconnect the main power source to the apparatus in the event of an emergency. Temporary wiring should only be used when absolutely necessary and must be replaced with permanent wiring as soon as possible. Temporary wiring must also comply with NEC codes. Extension cords must be used only as temporary wiring for portable equipment. For permanent equipment, permanent wiring should be installed.

(2) Grounding

All equipment should be grounded and fused in accordance with NEC codes.

(3) Insulation

All electrical equipment should be properly insulated. Any power cords that are frayed should be replaced and any exposed hot wires should be insulated to prevent the danger of electrical shock due to accidental contact. When working with high voltage equipment, properly rated gloves and matting for electrical protection should be used. When in doubt, consult with MIT's Electrical Services, part of physical plant.

(4) Isolation

All electrical equipment or apparatus that may require frequent attention must be capable of being completely isolated electrically. All power supplies must be enclosed in a manner that makes accidental contact with power circuits impossible. In every experimental setup, an enclosure should be provided to protect against accidental contact with electrical circuits. This applies to temporary arrangements as well.

(5) Personal Safety Techniques

A number of Safety Techniques can be found in the MIT Accident Prevention Guide # 3 located in the Chemistry Department Library of Lab Safety. In addition, the NEC handbook contains a section on electrical safety that should be read. The following safety procedures should always be followed:

- (a) Before servicing electrical equipment in any way its power source must be disconnected to avoid the danger of electrical shock.
- (b) Before reconnecting electrical equipment to its power source after servicing it is strongly recommended to test the equipment with a multimeter to assure that it is grounded.
- (c) Prudent electrical practices also suggest to properly fuse all electrical equipment to protect the user from electrical shock.

(6) Work with a partner who is trained in CPR

When installing, replacing, modifying, repairing, or rehabilitating any part of any electrical installation it is considered prudent practice to be with a person trained in CPR who can provide CPR if needed in case of an accidental electrical shock.

Section Four: Working with Lasers

A. Introduction

A laser is a device which when energized may emit visible and/or invisible coherent electromagnetic radiation. This radiation is emitted over a wide range of the electromagnetic spectrum and may be in the infrared, visible, or ultraviolet region. This radiation may be emitted continuously or in pulses. The radiation produced is non-ionizing, however, it may nonetheless cause injury if proper safety precautions are not observed. This is primarily due to the fact that many of today's lasers operate at extremely high power levels, high enough to permanently damage the eyes or skin in a single, momentary exposure. This guide will discuss some of the precautions that ***must be followed*** as well as some recommendations which ***should be followed*** for the safe use of laser equipment. **It is the responsibility of all researchers to be familiar with the health and physical hazards of the laser equipment involved in their work.**

Additional information is available from the MIT Radiation Protection Program (N52-496, 452-3477).

B. Laser Classification

<i>Class</i>	<i>Hazard Capabilities</i>
1	Cannot produce hazardous radiation.
2	Continuous intrabeam exposure damages the eye. Momentary intrabeam exposure (less than 1/4 sec) is not damaging to the eye. Visible radiation only.
3r	Eye damage may occur if the beam is viewed directly or with optical instruments.
3b	Eye and skin damage will occur from direct, momentary intrabeam exposure.
4	Can damage the skin as well as the eye during direct, momentary intrabeam exposure or exposure to diffuse reflections.

C. Registration of Laser Equipment

(a) Laser registration

All class 3b and 4 lasers must be registered with the MIT Radiation Protection Program (N52-496, 452-3477). Registration must be completed as soon as possible after a laser has been delivered to the research laboratory, and in any case before the laser is actually used. Registering the laser, which is the responsibility of the Principal Investigator (usually a faculty member) can be done from EHS website: <http://ehs.mit.edu/site> under the "Radiation Protection" tab and "Laser System Registration". Upon receipt of the completed form the RPP will conduct an inspection of the laser facility.

(b) Laser inspection

Before any new class 3b and 4 laser installation is cleared for use in experiments, it must be inspected and approved by the MIT Radiation Protection Program.

Any major change in the experimental set-up of a class 3r, 3b or 4 laser system, including moving the laser to a new location within MIT, will require re-inspection by a member of the MIT Radiation Protection Program.

D. Registration of Personnel Working with Class 3a, 3b, or 4 Lasers

Every laser user must attend a laser safety lecture at the Radiation Protection Program and be registered as a laser user with the Department of Chemistry. *No one* is permitted to operate or to participate in an experiment utilizing any class 3r, 3b or 4 laser without approval from the Radiation Protection Program and without being registered with the chemistry department. In addition, every laser user should obtain a laser eye examination (see below).

(a) Laser Safety Clearance Form

New members of the Department must submit a signed copy of the Laser Safety Clearance Form to Chemistry Headquarters prior to beginning work with any class 3r, 3b, or class 4 laser. The researcher must sign the section of the Laser Safety Clearance form that reads: "I have read and understand the contents of the Laser Safety Guide, and I am familiar with the hazards associated with the lasers used in my research. I have attended the laser safety lecture at the Radiation Protection Program, and I have had (or have scheduled) a laser eye examination on/for [date]". The section of the form that states "I have discussed laser safety with _____ and he/she is familiar with the hazards associated with the use of lasers in our laboratory" must be signed by the laboratory supervisor. New graduate students who are going to use lasers in their research are required to submit their Laser Safety Clearance Form by the end of January of their first year or when they first begin laboratory work (whichever comes first). Other research personnel (including postdocs, visiting scientists, technicians, and undergraduate students) must submit their Laser Safety Clearance Form within two weeks of the beginning of their appointment and before beginning work involving class 3r, 3b, or class 4 lasers. In the event that a completed form is not submitted on time, as required above, then the worker and their supervisor will be notified in writing by the Department Administrative Officer that the individual is not authorized to work in areas where class 3r, 3b, or class 4 lasers are in use. In addition, no person is allowed to use a laser unless authorized to do so by their laboratory supervisor.

(b) Laser Safety Lecture

All personnel whose work will involve the use of class 3r, 3b, or class 4 lasers are required to attend the laser safety lecture at the Radiation Protection Program. Attendance records will be maintained by the Radiation Protection Program.

(c) Laser Eye Examination

All personnel whose work will involve the use of a class 3r, 3b or class 4 lasers are recommended to obtain a laser eye examination. To obtain a laser eye exam at no cost, contact the MIT Eye Clinic (3-4351).

(d) Requirements to Operate Specific Laser Equipment

No person is to operate any laser for which they have not been specifically checked out by the EHS Representative and/or the Principal Investigator. A log book must be kept near each class 3 or 4 laser, and a list of qualified users must be attached to this log book in an easily visible location.

(e) Required Laser Safety Equipment

Every laser laboratory must have a collection of protective eye-wear available near the door of each room where laser light may exist. This collection must include sufficient quantities of separate sets of eye-wear designed for protection in each of the wavelength regions of class 3r, 3b, or 4 lasers in use at that location. In order to provide protection, the protective eye-wear must reduce the intensity of any incident beam to the level of a class 2 laser. If the protective eye-wear available

does not meet this criterion, flight tubes or other enclosures must be used to completely enclose the entire laser beam. Safety glasses which do not reduce diffuse reflections to the level of a class 2 laser are not considered safe and must not be used. See reference book “American National Standard for the Safe Use of Lasers” (by the Laser Institute of America) for ANSI code. It will not always be possible to protect researchers against all laser wavelengths in use at a given location with a single pair of laser goggles/glasses. In each location there must be at least one pair of safety glasses/goggles for each regular researcher working at that location that provides protection against the wavelength of laser light used. Additional pairs for visitors should also be available. This is especially important for rooms containing multiple lasers emitting multiple laser lines or single lasers emitting laser light, the wavelength of which can be altered in one or more places. If it is not possible to provide adequate protection against all wavelengths in use through the use of a single pair of laser safety glasses, then opaque light blocking dividers must be installed to protect researchers from accidental exposure to those laser lines against which their safety glasses do not offer protection.

Appropriate protective safety glasses/goggles must be worn at all times by all personnel working in the vicinity of any class 3 or class 4 laser emitting radiation that is not completely confined to a laser table or enclosed by suitable opaque protective material. Protective eye-wear is especially important for all workers in a laboratory in which adjustments are being made to an optical layout or in which it is normal procedure to insert or remove objects from the laser beam path. This includes personnel present in the same room, but not working with the laser. The use of protective eye-wear is suggested, but not required, if a light blocking divider, such as a thick, opaque, black, fire proof curtain or an equivalent thereof, is present and used to completely shield the location of the laser and its beam.

While any laser is operational, a lighted laser sign must be illuminated outside all entrances to the room. “Danger-Laser” signs may be obtained from the Radiation Protection Program. All laser laboratories must have locks on their doors to prevent unauthorized personnel, including Institute workers, from entering when lasers are operational. In addition, during alignment of a laser or laser beam path optics additional explicit warning signs must be posted on all entrances to that laboratory room to inform other personnel that they must not enter without wearing appropriate safety goggles.

All lasers must be equipped with safety interlocks and shields. Adequate exhaust ventilation systems must be operational and available, when appropriate, for the laser being used. Such systems often require additional approval by the Chemistry Department Chemical Hygiene Committee. (See Chemical Hygiene Plan and Safety Manual of the Department of Chemistry)

E. Working with Lasers

The most common, though not life threatening injuries caused by lasers are permanent eye damage and severe skin burns. These injuries tend to be caused by poor safety habits, inadequate safety equipment being worn by the researcher, operator error, inadequate safety precautions around the laser, and inadequate preparation by the researcher. The risk to other non laser workers in a laser laboratory can be greater than that to the laser user. A laser user must take responsibility for the safety of all workers in a laboratory. No beam manipulation procedure should be undertaken without explicit warnings to all workers and confirmation that the warning has been understood. It should be noted that almost all eye injuries involving lasers happen to personnel not wearing eye protection!!! In the event of a suspected injury, proceed to the MIT Medical Department for treatment. An accident report must be filed with the Chemistry Department (see Part IX) and the Radiation Protection Program.

In order to make the working environment around lasers as safe as possible and to minimize unforeseen events and to mitigate the effects of such events, the following safety procedures must be followed by all personnel operating or working around laser equipment.

(a) Procedures for the Safe Operation of Laser Equipment

Appropriate protective laser goggles/glasses must be worn by all personnel present in rooms in which class 3 or 4 laser light is being generated whenever that radiation is not totally confined to a laser table or totally enclosed. Protective eyewear must also be worn by all personnel present anytime adjustments are made to an optical layout involving a class 3 or 4 laser or when anyone is working near exposed class 3 or 4 radiation. A protective face shield or goggles must be worn at all times by all personnel in rooms in which class 3 or 4 UV or infrared radiation is being generated whenever that radiation is not totally enclosed.

Additional safety precautions must be followed for lasers emitting light other than visible, or experimental set-ups which convert visible laser light to the infrared or UV. To prevent accidental thermal burns and ignition of flammable materials, personnel or flammable materials must be kept out of the beam path. All beam stops/blocks must be made with materials such as firebrick or blackened metals that do not give off specular reflections. IR or UV cards, to view the IR or UV laser beam respectively, must also be available.

All laser beams must be kept either at the height of the laser table or near ceiling level (well above or well below the eye level of any standing observer), except when confined in flight tubes. No chairs, other than tall lab stools, should be present in laser laboratories. No beams not contained within flight tubes should be permitted to project upward above the laser table. General precautions with reference to beam aiming and the avoidance of specular reflections should be observed. No beam should ever be aimed, even temporarily, at any door. **All stray beams, regardless of intensity, leaving the confines of the laser table must be blocked.** An unsafe condition will be deemed to exist whenever laser beams, even secondary reflections, leave the area of the laser table not on a designated beam path. Laser beams crossing from one table to another should, if possible, be enclosed in flight tubes. Otherwise physical barriers or warning markers such as tape-marked safe-walking paths on the floor must be set up to keep personnel from accidentally walking into the beam.

The laser beam must be terminated at the end of its useful path by a material that is a diffuse matte of such color or reflectivity to make positioning possible while minimizing reflection. Such beam stops must be firmly attached to a solid support that cannot be moved accidentally.

All non-essential reflective material must be eliminated from the beam area and good housekeeping should be maintained. No jewelry, watches, belt buckles, wedding rings, etc. that could possibly enter the beam path should be worn by personnel working around lasers. Mirrors, mounts, tools, and other reflective pieces not part of an experimental set up must not be left on a laser table, but should be stored in another location to avoid accidental reflections from them. All laser mirrors and mounts must be firmly attached, by bolt or magnetic mount, to the laser table in such a way as to resist movement due to accidental contact in order to assure that the beam travels only along its intended path.

Shutters, attenuators, polarizers, or optical filters should be placed at the laser exit port to reduce the beam power to the minimal useful level.

The laser assembly should be designed to block radiation such as ultraviolet light generated by a gas discharge or light emitted from the jet of a dye laser. Also, flashlamps used in optically pumped systems should be shielded to eliminate any direct viewing.

All reflections of infrared or ultraviolet laser beams must be controlled by enclosure of the beam and target area. Ultraviolet laser beams must not cause scattered or diffuse reflected light in an area that could potentially expose workers.

No person is allowed to work alone with an energized laser or energized power supply without specific instructions and permission from their supervisor.

When aligning laser beams, it is suggested to work at as low a power as possible. For example in the case of Q switched YAG lasers, it may be possible to turn off the Q switching. The use of a video camera is strongly recommended if high power levels are necessary.

Walls and ceilings should be painted with non-gloss paint to produce a diffuse surface. Diffuse black is preferred.

Researchers must be aware of the “blue light” hazard. The threshold for eye damage is 100 times lower for blue light than for red or near-ultraviolet. For example, the diffuse reflection of a multiwatt argon ion laser beam falling on a black beam stop can be an eye hazard.

Wearing appropriate laser safety goggles/glasses will protect your eyes. However, there exist situations in which these goggles/glasses will not provide complete protection and eye damage will occur. **Never** look directly into a laser beam, even when wearing goggles/glasses!!! Goggles are designed to protect against momentary exposure and can bleach or melt if exposed to a direct beam (sometimes in a fraction of a second).

A laser SOP written by the laser users are required for Class 4 lasers and are recommended for Class 3 lasers.

F. Electrical Hazards

Electric shock is the most life threatening hazard encountered in work with lasers. There have been several electrocutions of individuals in the U.S. from laser-related electrical accidents. These accidents could all have been prevented.

(a) Procedures to Prevent Electric Shock when Working with Lasers

Part III of this Safety Manual must be read before doing any electrical work. The following general rules should always be followed:

- (1) Unplug and ground power supplies.
- (2) Avoid wearing rings, metallic watchbands, and other metallic objects which could come into electrical contact with exposed wires, capacitors, etc.
- (3) When possible, use only one hand when working on a circuit. Keep the other hand in your pocket.
- (4) Assume that all floors are conductive when working with the high voltages that are commonly encountered with lasers.
- (5) Check that each capacitor is discharged, shorted, and grounded before allowing access to the capacitor area. An accidental discharge of capacitors of the size frequently found in laser power supplies into the body can be lethal.
- (6) Inspect capacitor containers for deformations or leaks.

- (7) Safety devices such as rubber gloves, insulating mats, and grounding connectors must be available and used when necessary.
- (8) **NEVER** work on a laser power supply alone.
- (9) **NEVER** perform **any** work if doubt of personal safety exists.

Section Five: Working with Radiation and Radioactive Materials

A. Introduction

All work with radioactive materials and equipment that produces radiation (shorter than UV wavelength) is regulated by the Radiation Protection Program [RPP] (N52-496, 452-3477). The responsibilities of the Radiation Protection Program include:

1. Registration and instruction of radiation workers.
2. Personnel monitoring of internal and external radiation exposure.
3. Radioisotope laboratory inspections and radiation surveys.
4. Radioactive waste collection and disposal.
5. Environmental monitoring.
6. Leak-testing of sealed radioactive sources.
7. Monitoring of incoming and outgoing shipments of radioactive material.
8. Supervision of radiation emergencies, and special contamination operations.
9. Operation of an MIT vehicle for transportation of radioactive material.
10. Maintenance of radiation protection records.

In addition, the Radiation Protection Program staff is available for (a) consultation on laboratory design, shielding, and other radiation exposure control methods, and (b) presentation of lectures and training exercises on radiation protection techniques.

B. Procedures for Working with Radiation

All work with radioactive materials and radiation-producing equipment must be registered with the RPP. Specific procedures as well as application and registration forms may be found in the booklet, *Required Procedures for Radiation Protection*, available from the RPO.

Working with Radioactive Materials

1. Application for the possession and use of radioactive material must be made in writing to the RPP by the Laboratory Supervisor using Form RP-01.
2. All personnel using radioactive materials must register with the RPP and participate in a training seminar held by that office. Researchers are also required to pass an exam on the material presented in the training seminar. It is the responsibility of the Laboratory Supervisor to ensure that only registered researchers use radioactive material.
3. The Laboratory Supervisor must maintain an up-to-date inventory of all radioactive materials in use, where they are used, and who is authorized to use them.
4. Handling of radioactive materials must be carried out in accordance with instructions received by the RPP.
5. Radioactive materials must be maintained under lock and key at all times in accord with the requirements of the Radiation Protection Program.

Working with Radiation-Producing Equipment

This section applies to the use of x-ray diffraction equipment, fluorescence analysis equipment, and any other equipment that produces ionizing radiation. Specific procedures and registration forms for using this equipment can be found in the booklet *Analytical X-ray Equipment Safety Program* available from the RPP.

1. Laboratory supervisors must fill out an RP-81 form describing the proposed use of any radiation equipment. Approval from the Radiation Protection Program must be obtained before the equipment is operated.
2. All personnel using the equipment must register in writing with the RPP and receive specific training from them for the equipment used. It is the responsibility of the Laboratory Supervisor to ensure that only authorized, properly trained personnel use the equipment.
3. Use of radiation-producing equipment must be carried out in accordance with the instructions received by the RPP.

Emergency Telephone Numbers

Call 100 for emergency assistance in the event of fires, serious injuries, or chemical spills of particularly hazardous substances. Call 2-EHSS during daytime hours for access to the Environmental Health and Safety Office.

Campus Police	617-253-1212
Medical Department Emergencies	617-253-1311
Medical Department General Information http://web.mit.edu/medical/	617-253-4481
Operations Center (FIXIT)	617-253-4948
Safety http://web.mit.edu/environment/ehs/general_safety.html	617-452-3477
Industrial Hygiene http://web.mit.edu/environment/ehs/chemical_safety.html	617-452-3477
Biosafety http://web.mit.edu/environment/ehs/biosafety.html	617-452-3477
Radiation Protection http://web.mit.edu/environment/ehs/radiation.html	617-452-3477
Environmental Management http://web.mit.edu/environment/ehs/waste.html	617-452-3477