

# Safe Laboratory Practices in Chemistry

Harvey Mudd College  
Department of Chemistry

*Revised 31 March 2003*

Introduction .....	3
Formal Policy Statement .....	3
Information on Hazardous Substances .....	3
Protective Equipment .....	3
Eye Protection.....	3
Protective Apparel.....	4
Respirators.....	5
Laboratory Hoods.....	5
Fire Extinguishers, Safety Showers, and Eyewash Facilities.....	7
Standard Operating Procedures for Work with Hazardous Substances.....	8
Classes of Hazardous Substances.....	8
Carcinogens.....	9
Reproductive Toxins.....	11
Corrosive Substances.....	12
Irritants .....	12
Toxic and Highly Toxic Agents.....	12
Hazardous Substances with Toxic Effects on Specific Organs.....	12
Sensitizers.....	12
Flammable and Explosive Substances.....	12
General Procedures for Work with Toxic Substances .....	12
General Procedures for Work with Flammable and Explosive Substances.....	20
Chemical Storage.....	28
Procedures for Work with Particularly Hazardous Substances.....	29
Identification and Classification of Particularly Hazardous Substances.....	29
Select Carcinogens.....	29
Reproductive Toxins.....	30
Compounds with a High Degree of Acute Toxicity .....	31
Designated Areas.....	32
General Procedures for Work with Substances of Moderate to High Chronic Toxicity or High Acute Toxicity .....	33
Additional Procedures for Work with Substances of Known High Chronic Toxicity.....	35
Special Handling Procedures for Some Common Hazardous Substances.....	37
Prior Approval Requirements.....	48
Accidents and Emergencies.....	49
Glossary .....	50

## **Part I. Introduction**

### **A. Formal Policy Statement**

Harvey Mudd College is committed to providing a safe working environment and believes its employees and students have a right to know about health hazards associated with their work. This document is designed to inform you so you can make knowledgeable decisions about any personal risks. This document includes policies, procedures, and responsibility assignments designed to develop in you an awareness of potentially hazardous chemicals in the work place and to train you in appropriate, safe working conditions.

It is important that you assume responsibility for your own laboratory safety. The people who work in any given laboratory are best able to detect potential hazards in either the facility or in work procedures. When safety concerns arise, you are encouraged to contact your supervisor or instructor. Everyone will have access to pertinent safety information through their supervisor or instructor.

### **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 Chemistry Reading Room. Material Safety Data Sheets are another valuable source of information.

Material Safety Data Sheets (MSDS') are valuable sources of information on hazardous substances. An MSDS 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 MSDS to HMC the first time a compound is ordered by an employee. The Chemistry Department file of Material Safety Data Sheets is maintained in the Chemical Stockroom and any member of the Department can refer to this file and, if desired, obtain copies of any MSDS.

## **Part II. Protective Equipment**

This section 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 III and IV of this document for further discussion of work situations that require the use of protective equipment.

### **A. Eye Protection**

To minimize the risk of eye injury, HMC policy requires that all personnel, including visitors, wear eye protection at all times in Chemistry Department laboratories. This eye protection policy is necessary in order that HMC comply with Federal law (CFR 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.

Ordinary prescription glasses do not provide adequate protection against injury, and their use should be limited to providing minimal protection when you are present in the laboratory but not carrying out a chemical operation.

Safety glasses with side shields provide the minimum protection acceptable for regular use. Safety glasses must meet the American National Standards Institute standard Z87.1-1989 which specifies a minimum lens thickness (3mm), 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 therefore should 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 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 Safety Officer.

## **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 III and IV, work with certain chemicals and classes of chemicals requires that protective apparel such as lab coat or chemical-resistant apron be worn.
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 III-B).
4. Suitable gloves must always be worn when working with hazardous substances. Choose gloves made of material known to be (tested and found to be) resistant to permeation by the substance in use. 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.

5. Lab coats are to be worn only in the laboratory area and are to be buttoned. In areas where the potential for chemical splashes is great an impervious apron appropriate for the task will be worn.

### **C. Respirators**

It is HMC'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 protection 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. 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 a medical evaluation of all personnel intending to use a respirator. After an examination the physician will issue a "respirator user permit".
3. Personnel must participate in a Respirator Training Program prior to using a respiratory device. This training includes discussion of the proper use, maintenance, testing, cleaning, and storage of respiratory equipment.
4. All users must undergo fit testing when a respirator is first issued and subsequently as required by OSHA regulations.
5. Respiratory protection will be selected and used in accordance with Title 8 6150-5144.

### **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 types of local exhaust include vented enclosures for 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 any hazardous substance. In addition, a laboratory hood or other suitable containment device must be used for work with "particularly hazardous substances" (see Part IV). A properly operating and correctly used laboratory hood can control the vapors released from volatile liquids as well as dust and mists. Do not make any modifications to hoods or ductwork.

Do not use a laboratory hood for large pieces of equipment 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.

The Physical Plant annually inspects all laboratory hoods in the Chemistry Department. This inspection consists of measuring the face velocity of the hood and using a smoke stick to check its containment effectiveness visually. If the laboratory hood passes both the face velocity and smoke containment tests, then it is posted visually with an updated certification label. If the hood does not pass the survey and the problem is so severe that it is unsafe for use, then it is labeled with a "DO NOT USE" sign.

If the hood fails inspection due to a problem that the Physical Plant can correct (e.g. slipping fan belt, cracked duct work) then the Chemistry Department will submit a work order to have it repaired. Physical Plant will notify the Chemistry Department when the repairs have been completed and the hood has passed the survey. If a hood functions poorly due to incorrect use (e.g. clutter in the hood) then the Physical Plant will notify the Department Chemical Hygiene Officer. It is the responsibility of researchers and laboratory supervisors to notify the Physical Plant if any of their hoods do not have an updated certification label.

The average face velocity criteria used for hoods is 100 linear feet per minute. During inspections the hood face is divided into nine equal areas and the face velocity is measured in the center of these areas. Each measurement must be within 20 percent of the accepted face velocity criteria. The nine readings are averaged and the face velocity at the fully opened sash height is indicated on the survey label. If the face velocity average is less than 100 feet per minute, then the sash height that does produce a 100 feet per minute average will be found and the hood will be labeled with a line that indicates the maximum safe operating sash height. The sash will not be lowered below a reasonable working height (usually 20 inches); instead, an increase in airflow will be recommended. Once the face velocity measurements are completed, the containment tests are conducted on the hood with a smoke stick. The hood face is transversed with a smoke stick to observe the airflow patterns. No back flow which results in the release of smoke from the laboratory hood is permitted.

The type of hood and the physical condition is noted on the hood worksheet. If parts of the hood are missing such as the air foil or side panels, this will be noted. Removal of air foils usually produces a hood with unacceptable containment.

If there is any question about a laboratory hood's operation, then the Physical Plant should be called immediately. When a new laboratory hood is installed, it is the responsibility of the laboratory supervisor to ensure that no hazardous substances are used in the hood until it is surveyed and labeled by the Physical Plant. If any changes of any kind are made to the laboratory hood system, the Physical Plant should be notified so that a new hood inspection can be conducted.

Most laboratory hoods in the department are equipped with a fume hood monitor which provides information on the status of the system and allows the user some control of the hood operation. The diagram on the next page describes the key features of the fume hood monitor.

The following general rules should be followed when using laboratory hoods in the Chemistry Department:

1. 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 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 when on low fan mode. Keep the sash closed when not conducting work in the hood.
5. Do not clutter your hood with bottles or equipment. Keep it clear and clean. 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.

- Clean the grill along the bottom slot of the hood regularly so it does not become clogged with papers and dirt.
- Promptly report any suspected hood malfunctions to the Physical Plant.
- Use only chemical for which the quality of the available ventilation system is adequate.

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

*Prudent Practices for Handling Hazardous Chemicals in Laboratories*, National Academy Press, 1981, pp. 193-212.

*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.

Copies of the *J. Chem. Ed.* are on file in the Chemistry Department Conference Room.

## **E. Fire Extinguishers, Safety Showers, and Eyewash Facilities**

It is HMC policy that personnel are not required to extinguish fires that occur in their work areas. However, as discussed in Part V, under certain circumstances suitably trained personnel may attempt to extinguish fires. All laboratories in the Chemistry Department are provided with 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.

- Carbon dioxide extinguishers** are effective against Class B fires (involving burning liquids such as solvents) and Class C electrical fires. They are not effective against burning paper or trash fires. Do not use a CO<sub>2</sub> extinguisher against fires involving alkali and certain other metals (such as Al, Mg, Zn) and compounds such as lithium aluminum hydride.
- 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.
- 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.
- Met-L-X and Met-L-Kyl.** These extinguishers are effective against burning metals including 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 Physical Plant. Fire extinguishers are inspected and tagged annually by the Physical Plant.

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)). It is the responsibility of the Chemistry Laboratory Manager to inspect the portable fire extinguishers, safety showers, and eyewash facilities once each month. Safety showers and eyewash facilities are also inspected by the Physical Plant at least annually. In addition to the inspections by the Laboratory Curator, the HMC Safety 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, and eyewash facilities.

### **Part III. Standard Operating Procedures for Work 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 highly flammable pose another significant hazard in Chemistry Department laboratories. 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 IV. Select carcinogens (defined in detail in Part IV-A) include compounds for which there is evidence of carcinogenicity from studies involving experimental animals. These compounds should be handled using the general procedures for working with hazardous substances outlined in Part III-B 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: a-halo ethers

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

### Alkylating agents: sulfonates

- 1,4-butanediol dimethanesulfonate
- diethyl sulfate
- dimethyl sulfate
- ethyl methanesulfonate
- methyl methanesulfonate
- methyltrifluoromethanesulfonate
- 1,3-propanesulfone

### 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
- acryloein
- ethyl acrylate

### Acylation agents

- \*B-propiolactone
- B-butyrolactone
- dimethylcarbamoyl chloride

### Organohalogen compounds

- \*1,2-dibromo-3-chloropropane
- \*mustard gas (bis(2-chloroethyl)sulfide)
- \*vinyl chloride
- carbon tetrachloride
- chloroform
- 3-chloro-2-methyl propene
- 1,2-dibromomethane
- 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)
- 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), the Annual Report on Carcinogens published by the National Toxicology Program (NTP), and compounds known to be carcinogens to the State of California (listed under Prop. 65).

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 Toxins

Reproductive toxins are defined by the OSHA Lab Standard as including substances which cause chromosomal damage (mutants) and substances with lethal or teratogenic (malformation) effects on fetuses. Many reproductive toxins are chronic toxins which cause damage after repeated exposure or long-duration exposures with effects that become evident only after long latency periods.

Information on reproductive toxins can be obtained from Material Safety Data Sheets, by contacting the Director of Safety and Environmental Services, and by consulting the *Catalog of Teratogenic Agents*, Sixth Edition; Shepars, 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

acrylic acid	hexachlorobenzene
aniline	iodoacetic acid
cadmium	lead compounds
benzene	mercur compounds
carbon disulfide	nitrobenzene
N,N-	nitrous oxide
dimethylacetamide	
dimethylformamide	phenol
dimethylsulfoxide	polychlorinated and
diphenylamine	polybrominated
	biphenyls
estradiol	toluene
formaldehyde	vinyl chloride
formamide	xylene

The above list is not intended to be complete, and it is the responsibility of the researcher and the 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 in the first 8-12 weeks of pregnancy, a period which includes time when a woman may not know she is pregnant. Consequently, women of childbearing potential should take care to avoid all skin contact with chemicals. Pregnant women and women intending to become pregnant should consult with their laboratory supervisor with regard to the type of work they may safely perform and the special precautions they should take.

## (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), dehydrating agents (sulfuric acid, sodium hydroxide, phosphorous 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:

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

#### (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 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 or after exposure to a large dose of the substance. Examples of allergens include diazomethane, chromium, nickel, formaldehyde, isocyanates, arylhydrazines, benzylic and allylic halides, and 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 gas and heat.

### B. General Procedures for Work with Toxic Substances

Literally hundreds 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 document 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 Material Safety Data Sheets, and may involve discussions with the laboratory supervisor and the Director of Safety and Environmental Services.
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, and spill control materials. Be familiar with the location of the nearest fire alarm and telephone, and know the 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 III-A above that the majority of chemicals involved in research in Chemistry Department laboratories must be considered "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

HMC 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 III-A of this document.

### (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 II-B. It is advisable to wear a laboratory coat when working with hazardous substances. This is particularly important when wearing clothing such as shorts, miniskirts, and T-shirts that leave a significant area of skin exposed. In some cases laboratory supervisors may identify situations where the use of lab coats or more protective material 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 substance being used (see *Prudent Practices*, pp. 158-160).
- (b) Never use mouth suction to pipette chemicals or to start a siphon; a pipette bulb or aspirator should be used to provide vacuum.
- (c) Wash your hands with soap and water immediately after working with hazardous chemicals.
- (d) 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 II-C for a detailed discussion of laboratory hoods. OSHA Permissible Exposure Limits (PELs) and American Conference of Government Industrial Hygienists Threshold Limit Values (TLVs) should be observed when working with hazardous substances for which PELs and TLVs have been established. Never smell compounds of unknown toxicity.

### **(5) Equipment Maintenance**

Equipment should be inspected and maintained according to regular schedules. In particular, glassware used for operations involving hazardous substances should be carefully examined for cracks and flaws before use.

### **(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 one liter) must be stored below eye level.

- (e) Chemical storage refrigerators should be defrosted periodically and should not be overcrowded.

### **(7) Work Conducted Outside Normal Hours**

Researchers should avoid conducting work with hazardous substances when they are alone in the laboratory. When working alone, arrange with Campus Security or workers in other laboratories to check on you periodically. Some experiments are too hazardous to be conducted alone under any circumstances; it is the responsibility of researchers to consult with their supervisor to identify such particularly hazardous operations.

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 service such as electricity, cooling water, or 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.

### **(8) Children and Pets**

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 parents or other qualified adult.

### **(9) Storage of Hazardous Substances**

Researchers should refer to *Prudent Practices* pp. 225-229 for a discussion of procedures for storing chemicals in laboratories. All procedures employed must comply with OSHA regulations.

- (a) To avoid the accumulation of excess chemicals, always purchase the minimum quantities of commercial chemicals necessary for your research.
- (b) All containers of chemicals 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.
- (c) Only small quantities (less than 1 liter) of flammable liquids should be kept at work benches. Larger quantities should be stored in ventilated steel storage cabinets, preferably of the type described on page 227 of *Prudent Practices*. Quantities greater than 1 liter should be stored in metal or break-resistant containers.
- (d) Refrigerators used for storage of chemicals must be explosion-proof and laboratory-safe type units. Storage trays or secondary containment should be used to minimize the distribution of material in the event a container should break or leak.
- (e) Large containers (more than 1 liter) should be stored below eye level on low shelves. Never store hazardous chemicals on the floor.
- (f) Research groups should maintain an inventory list or card file of hazardous substances present in their laboratories.

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

## **(10) Transporting Hazardous Substances**

HMC policy requires that chemicals be transported between stockrooms and laboratories in break-resistant or approved secondary containers. Approved secondary containers are defined as commercially available bottle carriers made of rubber, metal, or plastic, with carrying handles and which are large enough to hold the contents of the chemical container in the event of breakage. When transporting cylinders of compressed gases, always strap the cylinder in a suitable hand truck and protect the valve with a cover cap.

## **(11) Disposal 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.

### **(a) Specific Procedures for Disposal of Excess and Waste Chemicals**

This section presents specific procedures for arranging for the disposal of the most common classes of excess and waste chemicals. Although many such chemicals can be removed from your laboratory without prior treatment, in some cases it is advisable to convert a substance into a less hazardous one prior to disposal. 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.

Disposal of excess and waste chemicals is scheduled by the Laboratory Manager and the Director of Safety and Environmental Services for once a month or more often if necessary. The Director of Safety will send a Physical Plant employee and truck to pick up and transport the materials to a special storage area maintained by the Physical Plant. Each container must be labeled properly. Unknown chemicals cannot be accepted for disposal by the Physical Plant. When the waste material is picked up, a packing list must be filled out providing information concerning the quantity and identity of the chemical and any hazards associated with it (flammable, toxic, water reactive, etc.).

### **(b) Liquid Organic Chemicals**

Local regulations that govern the HMC sanitary 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 solvent vapors. Excess and waste liquid organic chemicals should be stored in appropriate containers as outlined above and sent to the Physical Plant Waste Chemicals Storage Area. Compatible mixtures of liquid organic compounds can be stored in one container provided that the label 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). Etheral 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.



### **(c) Aqueous Solutions**

Aqueous solutions of acids and bases in the pH range of 5-9 can be disposed of by pouring them down the drain provided that they do not contain toxic contaminants such as certain heavy metal salts. Consult Chapter 6 of *Prudent Practices for Disposal of Chemicals from Laboratories* for a discussion of the toxicity hazards of various inorganic salts. Concentrated acids and alkalis should be neutralized and then disposed of down the drain.

### **(d) Solid Inorganic and Organic Chemicals**

Excess and waste solid chemicals can often be sent to the Physical Plant in their original containers. Compatible solids can be stored in one container provided that the label indicates the relative proportion of each component. Certain classes of solid waste chemicals require special handling. Toxic solid wastes can be sent to the Physical Plant in properly labeled, tightly sealed containers. Contact the Director of Safety for advice on the handling and packaging of toxic waste chemicals. Alkali metals such as sodium and potassium should be stored under mineral oil in tightly sealed containers and sent to the Physical Plant 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 Physical Plant for disposal. Waste mercury should be stored in the recycling containers to be sent for recycling. Broken thermometers that contain mercury should be placed in jars and also sent to the Physical Plant.

### **(e) Unknown Waste Chemicals**

The Physical Plant will not accept unknown chemicals for transport to the Waste Containment Storage Area. 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; in some cases this may require paying for the services of an outside analytical laboratory. Once the composition of the waste is known, it can be disposed of according to the procedures outlined above.

### **(f) Gas Cylinders**

Gas cylinders are not sent to the Physical Plant for disposal. Excess and empty gas cylinders should be brought to the Laboratory Manager who has the responsibility of returning cylinders to the proper vendor.

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

Radioactive materials (contact Annie Atiyeh x73940)

Polychlorinated biphenyls (contact The Director of Safety and Environmental Services x18538)

## **(12) Procedures for Handling the Accidental Release of Hazardous Substances**

It is HMC policy that when a spill occurs, the responsibility for having the spill cleaned up rests with the person causing the spill. If the individual responsible is unknown, or unable to clean up the spill due to injury, then responsibility for dealing with the spill rests with the Department. Custodians are not permitted to clean up spills of hazardous materials.

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 a spill does occur, the following General Guidelines for Handling Spills should be followed in the indicated order of priority.

1. Tend to any injured or contaminated personnel and if necessary request help (Campus Security x.72000).
2. Notify other personnel of the accident and if necessary evacuate the area.
3. Take steps to confine and limit the spill if this can be done without risk of injury or contamination.
4. Clean up the spill. Dispose of contaminated material properly according to the procedures described in section (10) of Part III-B 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 substance 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 available.

Department Spill Kits are available in the teaching laboratories and in the chemical stockroom. These kits are stocked with absorbent material, gloves, safety glasses and plastic bags. Contact the Laboratory Manager for replacement materials. In addition, other spill control materials are available in the chemical stockroom. These include brooms and mops, inert absorbents such as vermiculite and sand, and neutralizing agents for acid and alkali spills.

#### **(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 x72000, the Campus Security 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, removing any jewelry to facilitate removal of any residual materials. Check the MSDS 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, do not attempt to wipe the clothes. Quickly remove any 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 fifteen 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 fifteen 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 a 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 some cases (e.g. incidents involving the release of highly toxic substances and spills occurring in non-laboratory areas) it may be appropriate to activate the fire alarm to alert personnel to evacuate the building. Call x72000 to obtain emergency assistance.

### (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, toxic gas), and the degree and type of toxicity. Outlined below are some general guidelines for handling several common spill situations.

- 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 and (if necessary) shoe-coverings. Neutralize the spilled chemicals with materials such as sodium bisulfite (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-B, 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 petroleum 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 vermiculite or other absorbent. 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 and contact the Chemical Hygiene Officer and Campus Security. The Claremont Fire Department has special 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, 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 agents.** 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.** These 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 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 Security (dial x2000) to obtain emergency assistance.

### C. General Procedures for Work with Flammable 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.

Compound	Flash Point (°C)	Compound	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.
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 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.

## 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 handling 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 more sensitive to heat, friction, impact, light, as well as strong oxidizing 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 auto oxidation 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 (tetrahydromaphthalene).

(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. Do not attempt to open bottles of liquid ethers (e.g. diisopropyl ether) containing crystallized material; contact the Chemical Hygiene Officer for assistance.

Before distilling any known or suspected peroxide-former, check it carefully for the presence of peroxides. 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 (25g 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.

For assistance in disposing of larger quantities of peroxides or other explosive materials, contact the Director of Safety and Environmental Services.

## Control of Fires

HMC policy states that personnel are not required to fight fires. The following guidelines should be followed to prevent and minimize injury and damage from fires.

1. **Be prepared!** Know where all of the fire extinguishers are located in your 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. **Fire in small vessels** can usually be suffocated by loosely covering the vessel. Never pick up a flask or container of burning material.
3. **A small fire which has just started** can sometimes be extinguished with a laboratory extinguisher. Extinguishing such fires should only be attempted if you are reasonably confident the 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.

4. **Small fires involving reactive metals and organometallic compounds** (such as magnesium, sodium, potassium, metal hydrides, etc.) should be extinguished with Met-L-X or Met-L-Kyl extinguishers (see Part IV section E), or by covering with dry sand.
5. **In the event of a more serious fire**, evacuate the laboratory and activate the nearest fire alarm. Be prepared to meet and advise the Fire Department and Emergency Response Team with regard to what hazardous substances are present in your laboratory.
6. **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 cloths 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 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.

**Acetylinic compounds** are explosive in mixtures of 2.5 - 80% with air. At pressures of 2 or more atmospheres, acetylene subjected to an electrical discharge in 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 air rapidly condense liquid air. When the coolant is later removed and 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.

**Oxygen tanks.** Serious explosions have resulted from contact between oil and high-pressure oxygen. Oil should not be used on connections to any oxygen cylinder.

**Ozone** is 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.

**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 reactions 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.



**Parr bombs** used for hydrogenation have been known to explode. They should be handled with care behind shields, and the operator should wear goggles.

**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. 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. Perchloric acid evaporations should be carried out in a hood that has a good draft and a built-in water spray for the duct work 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.

**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.

**Peroxides (inorganic).** When mixed with combustible materials, barium, sodium, and potassium peroxides form explosives that ignite easily.

**Phosphorous (red and white)** forms explosive mixtures with oxidizing agents. White P should be stored under water because it is spontaneously flammable with air. The reaction of P with aqueous hydroxides produces highly toxic phosphine, which may ignite spontaneously in air or explode.

**Phosphorous 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.

**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.

**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.

**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 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 serious explosion or in 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	Water, carbon tetrachloride or other chlorinated hydrocarbons, carbon dioxide, halogens
Ammonia (anhydrous)	Mercury (in manometers, or 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	Acetic acid, maphthalene, camphor, glycerol, trioxidealcohol, flammable liquids in general
Chlorine	Ammonia, acetylene, buradiene, burane, methane, propane (or other petroleum gases), hydrogen, sodium carbode, benzene, finely divided metals, turpentine
Chlorine dioxide	Ammonia, methane, phosphine, hydrogne sulfide
Copper	Acetylene, hydrogne peroxide
Cumene hydroperoxide	Acids (inorganic or organic)
Cyanides	Acids
Decaborane	Carbon tetrachloride and some other halogenated hydrocarbons
Flammable liquids	Ammonium nutrate, chromic acid, hydrogen peroxide, nitric acid, sodium peroxide, halogens
Fluorine	Everything
Hydrocarbons	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, amiline, nitromethane, combustible materials
Hydrogen sulfide	Fuming nitric acid, oxidizing bases
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	Acetic anhydride, bismuth and its alloys, alcohol, paper, wood, grease, oils
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
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 nitrate	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 and lithium
Tellurides	Reducing agents

#### D. Chemical Storage

The amount of chemicals stored in laboratories is to be kept as small as is practical. Storage on bench tops and in hoods presents the potential for exposure to fire and spills. Ventilated cabinets and specially monitored refrigerators should be used for chemical storage only. Flammable liquids should be stored in flammable storage cabinets with self-closing doors and proper ventilation. Toxic chemicals, including carcinogens, should be stored in ventilated areas in unbreakable, chemical resistant secondary containers. Cylinders of compressed gases should be strapped or chained to a wall or bench top and should be capped when not in use or during transportation.

## Part IV. Procedures for Work with Particularly Hazardous Substances

### A. Identification and Classification of Particularly Hazardous Substances

As discussed in the previous section, 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*”. The OSHA Laboratory Standard requires that special provisions be established to prevent the harmful exposure of researchers to PHS’. General procedures for working with such materials are presented in detail in Parts IV-C and IV-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 IV-C below. Note, however, that in some circumstances (e.g. when very small quantities of materials are being used) it may not be necessary to employ all of the special precautions described in Part IV-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’. 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 carcinogenic” 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/m<sup>3</sup>; (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 some of 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 NTP lists.

## Partial List of Select Carcinogens

2-acetylaminofluorene	dimethylaminoazobenzene
acrylonitrile	ethylene oxide
4-aminobiphenyl	ethylenimine
amalgamic mixtures containing phenacetin	formaldehyde
arsenic and certain arsenic compounds	melphalan
asbestos	methoxsalen with ultraviolet A azathioprine
benzene	4,4'-methylene-bis(2-chloroaniline)
benzidine	mustard gas
betel quid containing tobacco	N,N'-bis(2-chloroethyl)-2-naphthylamine (chlornaphazine)
bis(chloromethyl) ether	□-naphthylamine
1,4-butanediol dimethylsulfonate	□-naphthylamine
chlorambucil	4-nitrobiphenyl
chloromethyl methyl ether	N-nitrosodimethylamine
chromium and certain chromium compounds	□-propiolactone
coal-tar pitches	shale oils
coal tars	smokeless tobacco products
conjugated estrogens	soots and soot extracts
1,2-dibromo-3-chloropropane	thorium oxide
3,3'-dichlorobenzidine (and its salts)	tobacco smoke
diethylstilbestrol	treoculphan
vinyl chloride	

**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 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 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 laboratory supervisor and the Director of Safety before working with substances that are suspected to be reproductive toxins. As minimal precautions, the general procedures outlined in Part IV-C below should then be followed.

Information on reproductive toxins can be obtained from the MSDS, by contacting the Director of Safety, 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 of the 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

acrylic acid	hexachlorobenzene
aniline	iodoacetic acid
benzene	lead compounds
cadmium	mercury compounds
carbon disulfide	nitrobenzene
N,N-dimethylacetamide	nitrous oxide
dimethylformamide (DMF)	phenol
dimethyl sulfoxide (DMSO)	polychlorinated and
diphenylamine	polybrominated biphenyls
estradiol	toluene
formaldehyde	vinyl chloride
formamide	xylene

**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, hepatotoxins, nephrotoxins, neurotoxins, agents that act on the hematopoietic systems, and agents which damage the lungs, skin, 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 defined as "toxic" and "highly toxic" agents in 29 CFR 1910.1200 Appendix A (see table below), and substances which "may be fatal or cause damage to target organs as the result of a single exposure or exposures of short duration".

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

#### Partial List of Compounds with a High Degree of Acute Toxicity

acrolein	hydrogen chloride
acrylic acid	hydrogen cyanide
acrylonitrile	hydrogen fluoride
allyl alcohol	hydrogen sulfide
allylamine	methyl fluorosulfonate
bromine	methyl iodide
chlorine	nickel carbonyl
diazomethane	nicotine
diborane (gas)	nitrogen dioxide
1,2-dibromoethane	osmium tetroxide
dimethyl sulfate	ozone
ethylene oxide	phosgene
hydrazine	sodium azide
hydrogen bromide	sodium cyanide (and other cyanide salts)

**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 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 IV-C below. Note, however, that in some circumstances (e.g. when very small quantities of materials are being used) it may not be necessary to employ all of the special precautions described in Part IV-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 Chemical Hygiene Committee before work with them can be carried out. See Part V 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 compounds. 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 underscored 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 becomes saturated, 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, 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 Lab Standard is that all work with particularly hazardous substances be confined to designated areas. A designated area is defined as a laboratory, an area of a laboratory, or a device such as a laboratory hood that is posted with warning signs that ensure that all employees working in the area are informed of the hazardous substance in use there.

It is the responsibility of the laboratory supervisor 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”. In some cases it may be appropriate to post additional signs describing unusual hazards present and/or identifying the specific hazardous substance 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 in laboratory hoods.

### **C. General Procedures for Work 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 IV-D below. Keep in mind that all of the general rules for working with toxic substances discussed in Part V-B of this document 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 IV-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 (see *Prudent Practices*, pp. 158-160) of 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 area 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 clean up 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 Director of Safety and Environmental Services and Campus Security should be contacted for assistance and equipment for spill clean up. 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 III-B 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 III-B 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 appropriate 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 substances in use in their laboratories. In addition, records that include amounts of materials used and names of workers involved should be kept as part of the laboratory notebook record of all experiments involving particularly hazardous substances. Record the average amount of each substance stored in the laboratory on a monthly basis, as well as the physical state (gas, liquid, solid) and the NFPA hazard classification if known.

## **(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 IV-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 Work 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.

### **(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 or not all plans for experimental operations and waste disposal. In addition, note that prior approval from the Chemistry Department Chemical Hygiene Committee is required for work with certain extremely hazardous substances (see Part V).

### **(2) Restrict Access to Areas Where Substances of High Chronic Toxicity Are Being Used and Stored**

All volatile substances having high chronic toxicity should be stored in a ventilated storage area in a secondary tray or container having a sufficient capacity to contain the material should the primary container accidentally break. All containers of substances in this category should have warning 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 IV-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 the surrounding area (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 of 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 (see *Prudent Practices*, pp. 158-160). Two gloves should generally be worn on each hand. In the event of an accident, the outer glove 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, arms, face, and neck. If disposable apparel or absorbent paper liners have been used, these items should be placed in a closed and impervious container that should then be labeled in some manner such as the following: CAUTION: CONTENTS CONTAMINATED WITH SUBSTANCES OF HIGH CHRONIC TOXICITY. Non disposable protective apparel should be thoroughly washed, and containers of disposable apparel and paper liners should be incinerated.

### **(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  $\gamma$ -propiolactone, bis(chloromethyl)ether, or methyl chloromethyl ether have been used should be treated for 10 minutes 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 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 Director of Safety 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 Director of Safety and Environmental Services 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 VII for a further discussion of medical surveillance.

### **E. Special Handling Procedures for Some Common Hazardous Substances**

This section outlines special handling procedures for some specific particularly hazardous substances that may be 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 human carcinogen by OSHA and also is listed as a substance with a high degree of acute toxicity. The PEL (permissible exposure limit) is 2 ppm as an 8-hour time-weighted average or 10 ppm as averaged over any 15 minute period. Skin contact with liquid acrylonitrile is also prohibited. Work involving significant quantities of acrylonitrile should be conducted using the general procedures outlined in both Parts IV-C and IV-D. Laboratory hoods that have been demonstrated to provide sufficient protection should be used, and closed systems are recommended for laboratory operations.

#### **(2) Benzene**

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 includes 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, bruising, or hematuria. Severe cases may have fatal outcomes. Recently, a number of reports 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. 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 IV-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: LD<sub>50</sub> (rats, 7-hour inhalation) = 7 ppm. It is moderately toxic via the oral and skin routes: LD<sub>50</sub> (rats, oral) = 280 mg/kg; LD<sub>50</sub> (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. 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 (1ppb; 5 mg/m<sup>3</sup>). 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 IV-C and IV-D.

### **(4) Carbon Monoxide**

Carbon monoxide is a direct and cumulative poison. It combines with the hemoglobin 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. The gas is a treacherous poison because of its odorless character and insidious action. 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.

Carbon monoxide should be used only in areas with adequate ventilation employing the general procedures outlined in Part IV-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 TLV (threshold limit value) for carbon tetrachloride are 5 ppm as an 8-hour time-weighted average, 25 ppm as a ceiling for any period of time provided the 8-hour average is not exceeded, and 200 ppm for 5 minutes in a 4-hour period. In 1980 the ACGIH proposed a change to 5 ppm for an 8-hour time-weighted average and a ceiling exposure level of 20 ppm for up to 15 minutes on the basis that carbon tetrachloride is suspected to have carcinogenic potential in humans. ACGIH also states that skin contact may account for a substantial part of the toxic responses.

The carcinogenic potency of carbon tetrachloride is low and 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 IV-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 toxic effects and its volatility. Nitrile rubber is the recommended material for gloves and other protective clothing.

## **(6) Chlorine**

Chlorine is classified as a substance with a high degree of acute toxicity. Humans can generally detect the odor of chlorine at about 0.3 ppm; at a range of 2.6-41.0 ppm, a group of "trained industrial hygienists" noted "strong irritation". The subjective response to chlorine is less pronounced with prolonged exposure. Experimentally determined responses to chlorine by humans are not very consistent. Throat irritation occurs at about 6.6-15 ppm. However, an exposure for medical purposes of a large number of humans to 5-7 ppm for 1 hour did not result in serious or long-term consequences. Exposure to about 17 ppm causes coughing, and levels as low as 10 ppm may cause lung edema. Chronic effects on humans from long-term low-level exposures have been well documented. Animal exposures have indicated that prolonged exposure to approximately 1.7 ppm for 1 hour per day may cause deterioration in the nutritional state, blood alteration, and decreased resistance to disease. The TLV and the OSHA PEL are 0.5 ppm (3 mg/m) as a ceiling. NIOSH has recommended a ceiling limit of 0.5 ppm over any 15 minute period. The ACGIH 15-minute limit is 3 ppm.

Chlorine should be kept away from easily oxidizable materials. Chlorine reacts readily with many organic chemicals, sometimes with explosive violence. Because of its high toxicity, laboratory operations using chlorine must be carried out in a hood employing the general procedures outlined in Part IV-C.

## **(7) Chloroform**

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 possible 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.

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

phosphorous pentoxide, potassium hydroxide plus methanol, potassium tert-butoxide, sodium, sodium hydroxide plus methanol, sodium methylate, and sodium hydride.

The current OSHA PEL 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-minute 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 IV-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 hour. 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 minutes was fatal. DMS is moderately toxic to animals via the oral route; LD<sub>50</sub> (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 has 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 for DMS is 0.1 ppm (0.5 mg/m<sup>3</sup>) as an 8-hour time weighted average. DMS is classified as being suspected of carcinogenic potential in humans by the ACGIH. The OSHA PEL for DMS is 1.0 ppm. These limits include a warning of the potential contribution of skin adsorption to the overall exposure.

The general procedure outlined in Part IV-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 quantities of vapor by working in a hood. Operations involving smaller quantities of DMS can be conducted using the general procedures presented in Part IV-C.

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

Ethylene Dibromide (EDB) is classified as a compound with a high degree of acute toxicity; the approximate oral lethal dose of EDB for humans is 5 mL. Skin adsorption 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 300 ppm for 6 minutes, 400 ppm for 30 min, and 200 ppm for 2 hours. It is moderately toxic via the oral and skin routes; LD<sub>50</sub> (rats, oral) = 140 mg/kg; LD<sub>50</sub> (rabbits, skin) = 300 mg/kg. EDB is markedly



irritating to skin, and a 10% solution has caused serious but reversible corneal injury to 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 for EDB was 20 ppm (155 mg/m<sup>3</sup>) as an 8-hour time-weighted average. The exposure limit is 30 ppm over any 15-minute 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, but the ACGIH recommends that those working with A 1b carcinogens should be properly equipped to ensure virtually no contact with the carcinogens. The OSHA PEL for EDB is 20 ppm, and the acceptable maximum peak is 50 ppm for 5 minutes in any 8-hour time period.

On the basis of the carcinogenicity data for EDB, the procedures described in Part IV-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 IV-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; LC<sub>50</sub> (rats, 4-hour inhalation) = 570 ppm; LD<sub>50</sub> (rats, oral) = 60 mg/kg; LD<sub>50</sub> (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 findings 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 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 for hydrazine is 0.1 ppm (0.1 mg/m<sup>3</sup>) and the OSHA PEL is 1.0 ppm (1 mg/m<sup>3</sup>) as 8-hour time-weighted average. 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 IV-C and IV-D should be used because hydrazine is carcinogenic in animal tests, quite volatile, and readily absorbs 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 HBr and 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 humans 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 result in dermatitis. Contact with the eyes rapidly causes irritation of the eyes and eyelids.

Hydrogen bromide and hydrogen chloride are corrosive gases that have pungent, irritating odors. 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<sup>2</sup>) for HCl and 2.20 MPa (320 lb/in<sup>2</sup>) 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 IV-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 V).

## (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 ulcers.

When handling HF, it is crucial to ensure adequate ventilation by working only in a hood so that safe levels (3ppm) 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 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 in water and toxic). Alternately, 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 a small hole in a glove, application of a calcium gluconate antidote gel can bind free fluoride ion not removed by washing.

If HF liquid or vapor has contacted 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 ounces of milk of magnesia to drink to soothe the burning effect.

#### (14) **Hydrogen Sulfide**

Hydrogen sulfide is extremely dangerous. Human exposure to relatively low concentrations of H<sub>2</sub>S has caused corneal damage, headache, sleep disturbances, nausea, weight loss, and other symptoms suggestive of brain damage. Higher concentrations can cause irritation of the lungs and respiratory passages and even pulmonary edema. Exposure to 210 ppm for 20 minutes has caused unconsciousness, arm cramps, and low blood pressure. Coma may occur within seconds after one or two breaths at high concentrations and may be followed rapidly by death. For example, workers exposed to 930 ppm hydrogen sulfide for less than 1 minute died. Hydrogen sulfide is moderately toxic to animals via the inhalation route; LC<sub>50</sub> (mice, 1 hour) = 673 ppm; LC<sub>50</sub> (mice, 7.5 hours) = 140 ppm. Exposure to 10-13 ppm for 4-7 hours has caused eye irritation. Skin adsorption of hydrogen sulfide is slight and not considered significant. However, prolonged or repeated skin contact might cause mild irritation. Guinea pigs that had 0.78 in<sup>2</sup> of their skin exposed to 100% hydrogen sulfide vapors for 1 hour experienced slight swelling. The TLV for hydrogen sulfide is 10 ppm (14 mg/m<sup>3</sup>) as an 8-hour time-weighted average. The short-term exposure limit (15 minutes) is 15 ppm. The OSHA PEL has a ceiling limit of 20 ppm and a peak of 50 ppm over any 10-minute period. NIOSH (1977) has recommended a 10-minute ceiling of 10 ppm.

Partly because of the disagreeable odor of hydrogen sulfide, but also because of its toxicity, laboratory operations with it should be carried out in a hood. Use the general procedures outlined in Part IV-C when working with hydrogen sulfide. Cylinders of it should not be stored in small, unventilated rooms, as deaths have resulted from people entering such rooms containing a leaking cylinder.

#### (15) **Nickel Carbonyl**

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

#### (16) **Nitrogen Dioxide**

Nitrogen dioxide 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. One hundred ppm of nitrogen dioxide in air is a dangerous concentration for even a short exposure, and 200 ppm may be fatal in a short time. 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, 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 IV-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 mg of mercury per cubic meter of air or 2.4 ppm of air. The ACGIH has established a TLV for mercury vapor of 0.05 mg/m<sup>3</sup> for continuous 40-hour per week exposure. Long term chronic exposure to mercury vapor in excess of 0.05 mg/m<sup>3</sup> 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 mercury 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 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 IV-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.

**Cleanup 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 Chemical Hygiene Officer will survey the area and advise on the degree of hazard which may exist and necessary preventative measures to be undertaken. 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 mercury from laboratory devices 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 in a safe manner.

## (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, including subprimates. 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 upon exposure.

The general procedures outlined in Parts IV-C and IV-D should be followed when working with N-nitrosodialkylamines. All work with these materials 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 container; storage should be in a ventilated storage cabinet (or in a hood).

**Cleanup of Spills and Waste Disposal** -- Because N-nitrosodialkylamines are chemically stable under usual conditions, disposal is best carried out by incineration. Contact the Director of Safety to arrange for 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 wastes. 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-nitrosodialkylamine can be absorbed by a commercial spill absorbent. After the absorbent 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 Campus Security 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 are dryness 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 minutes 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, 47% of a group of rats died from exposure to 55-100 ppm for only 10 minutes. 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 and the OSHA PEL for phosgene are 0.1 ppm (0.4 mg/m<sup>3</sup>) as a 8-hour time-weighted average. NIOSH has recommended a limit of 0.2 ppm over any 15-minute period.

Laboratory operations involving phosgene require the use of the general procedures outlined in Part IV-C. Work with phosgene should always be carried out in 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 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; LD<sub>50</sub> (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 adsorbtion and inhalation. The TLV and the OSHA PEL for cyanide are both 5 mg/m<sup>3</sup> as an 8-hour time-weighted average. These limits include a warning about the potential contribution of skin absorption to the overall exposure. In 1976, NIOSH recommended that the 5 mg/m<sup>3</sup> limit be retained but that its basis be changed from an 8-hour TWA to a 10-minute 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 IV-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 notify 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 Director of Safety 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 V. Prior Approval Requirements

The use of certain particularly hazardous substances requires the prior approval of the Chemistry Department Chemical Hygiene Committee. At the time of this writing, prior approval is required for work with the compounds listed below. Additions to this list will be posted in the Chemistry Department Office.

### Restricted Chemicals Requiring Prior Approval

Fluorine  
Hydrogen cyanide  
Hydrogen fluoride  
(anhydrous)  
Nickel carbonyl

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 Chemical Hygiene Committee. This plan should specify:

1. Procedures for routine handling and storage of the restricted material.
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 the Chemistry Department Chemical Hygiene Officer.



## Part VI. Accidents and Emergencies

### A. Emergency Procedures

1. Call Campus Security at extension 2000 to obtain assistance in the event of an emergency. Report the nature and location of the emergency, including both your building and floor number.
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 to leave the building.**
3. Procedures for handling the accidental release of hazardous substances are discussed in Part III-B.
4. Procedures to follow in the event of a fire are discussed in Part III-C.
5. If a co-worker has ingested a toxic substance, have the victim drink large amounts of water while escorting them to a safe, quiet location. Attempt to learn exactly what substances were ingested and inform emergency medical staff as soon as possible.
6. In case of eye contact, promptly flush with water for fifteen minutes and seek medical attention.
7. In case of skin contact, promptly flush with water for fifteen minutes, removing clothing contaminated with the substance. Use a safety shower if the contact is extensive. If symptoms persist after washing, seek medical attention.
8. If a co-worker 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.
9. Do not touch a person in contact with a live electric circuit - disconnect the power first!

## VII. Glossary

The following terms are used in this document:

ACUTE	An adverse effect with symptoms of high severity coming quickly to a crisis.
CARCINOGEN	A substance capable of causing cancer.
CHRONIC	An adverse effect with symptoms that develop slowly over a long period of time or that frequently recur.
COMBUSTIBLE	Able to catch on fire and burn.
DOT	Department of Transportation
EMPLOYER	The party legally responsible for administration, policy, and management of the business.
EPA	Environmental Protection Agency
FLAMMABLE	Capable of being easily ignited and of burning with extreme rapidity.
INFECTIOUS AGENTS	Sources that cause infections either by inhalation, ingestion, or direct contact with the host material.
LABORATORY SCALE	Work with chemicals that can easily and safely be manipulated by one person excluding the commercial production of chemicals for sale.
LABORATORY USE	A work place where relatively small quantities of hazardous chemicals are used on a non-production basis.
LC <sub>50</sub>	The concentration of a substance in air that causes death in 50% of the animals exposed by inhalation. A measure of acute toxicity.
LD <sub>50</sub>	The dose that causes death in 50% of the animals exposed by any route other than inhalation of the substance. A measure of acute toxicity.
MSDS	Material Safety Data Sheet
MUTAGEN	Capable of changing cells in such a way that future cell generations are affected. Mutagenic substances are usually considered suspect carcinogens.
OSHA	Occupational Safety and Health Administration. The regulatory branch of the Department of Labor concerned with employee safety and health.
PEL	Permissible Exposure Limit. The legally allowed concentration in the work place that is considered a safe level of exposure for an 8-hour shift, 40 hours per week.

pH	A measure of how acidic or caustic a substance is on a scale of 1 to 14. A pH of 1 indicates that a substance is acidic; a pH of 14 indicates that a substance is basic.
PHYSICAL AGENTS	Work place sources recognized for their potential effects on the body. Heat exposure or excessive noise levels are examples of this risk group.
SENSITIZERS	Agents to which exposure over time creates an allergic reaction at some point in time.
STERILITY	Changes made in male or female reproductive systems resulting in inability to reproduce.
TERATOGEN	A substance that causes a deformity in new-borns if a significant exposure exists during pregnancy.
TLV	Threshold Limit Value. That amount of exposure allowable for an employee in an 8-hour day.