University of South Carolina Department of Chemistry & Biochemistry

# **Chemical Hygiene Plan and Safety Manual**

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Department of Chemistry & Biochemistry Safety Information web site: http://www.chem.sc.edu/faculty/morgan/safety/

USC Environmental Health & Safety web site: <u>http://ehs.sc.edu/</u>

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Copies of this Chemical Hygiene Plan are available for downloading, in either Microsoft Word® or Abode Acrobat® format, from the USC Chemistry and Biochemistry safety web site at URL:

http://www.chem.sc.edu/faculty/morgan/safety/

# **Chemical Hygiene Plan**

		Page
	Document Downloading Information	2
I.	Information Sheets, General Guidelines, and Forms	7
	Emergency Contact Information	8
	General Guidelines for Chemical Safety and Security	9
	Chemical Hygiene Clearance Form	10
	Laboratory checklist	11
	Accident/Incident Report Form	12
	Fume hood clearance food to be filed for hood repair requests	13
II.	Introduction	14
	A. Policy	14
	B. Purpose	14
	C. Personnel covered by this plan	14
	D. Acknowledgment	14
III.	Responsibility, Authority, and Resources	15
	A. Department Chair	15
	B. Safety Committee and Chemical Hygiene Officer	15
	C. Laboratory Supervisors	16
	D. Group Safety Officers	17
	E. Employees, Staff, and Research Personnel	17
	F. Department of Chemistry & Biochemistry Stockroom	18
	G. Health & Safety Programs Unit, Occupational Health Services,	
	and Thomson Student Health Center.	18
IV.	Information and Training	19
	A. Initial Training	19
	B. Hazard Identification	20
	C. Container Labeling	22
	D. Material Safety Data Sheets (MSDS) and Internet Resources	23
	E. Chemical Inventory	24
V.	Protective Equipment	25
	A. Eye Protection	25
	B. Protective Apparel	26
	C. Respirators	26
	D. Laboratory Hoods	27
	E. Fire Extinguishers, Safety Showers, and Eyewash Facilities	28
VI.	Standard Operating Procedures for Work with Hazardous Substances	30
	A. Exposure Guidelines	30

B	Classes of Hazardous Substances	Page
D.	(1) Carcinogens	31
	(2) Reproductive toxins	34
	(3) Corrosive Substances	35
	(4) Irritants	35
	(5) Toxic and Highly Toxic Agents	35
	(6) Hazardous Substances with Toxic Effects on Specific Organs	35
	(7) Sensitizers	36
	(8) Flammable and Explosive Substances	36
C.	General Procedures for Work with Toxic Substances	36
	(1) Eye protection	37
	(2) Personal apparel	37
	(3) Avoid skin contact and ingestion	37
	(4) Avoid inhalation of toxic substances	37
	(5) Equipment maintenance	37
	(6) Housekeeping	38
	(7) Work conducted outside normal hours	38
	(8) Children and pets in laboratories	39
	(9) Storage of hazardous substances	39
	(10) Transporting hazardous substances	39
	(12) Procedures for handling the accidental release of hazardous substances	39 41
D.	General Procedures for Work with Flammable and Explosive Substances	44
	(1) Handling Flammable Substances	44
	(2) Handling Explosive Substances	45
	(3) Control of Fires	46
	(4) Personal injuries involving fires	46
	(5) Specific Hazards That May Lead to Fires or Explosions	47
	(6) Incompatible chemicals	49
Pro	cedures for Work with Particularly Hazardous Substances	52
A.	Identification and Classification of Particularly Hazardous Substances	52
	(1) Select Carcinogens	52
	(2) Reproductive toxins	54
	(3) Compounds with a High Degree of Acute Toxicity	54
В.	Designated Areas	55
C.	General Procedures for Work with Substances of Moderate to High	
	Chronic Toxicity or High Acute Toxicity	57
	(1) Information	57
	(2) Zero skin contact	57
	(3) Use laboratory hoods	57
	(4) Be prepared for accidents	57
	(5) Don't contaminate the environment	58
	(b) Record keeping (7) Protected and a second keeping	58
	(1) Restrict access to areas where particularly hazardous substances are in use	58

VII.

	<ul> <li>D. Additional Procedures for Work with Substances of Known High Chronic Toxicity <ol> <li>(1) Approvals</li> <li>(2) Restrict access to areas where substances of high chronic toxicity are being used or stored</li> <li>(3) Wear suitable personal protective apparel</li> <li>(4) Protect the environment and dispose of waste materials properly</li> <li>(5) Be prepared for accidents</li> <li>(6) Medical surveillance</li> </ol> </li> <li>E. Special Handling Procedures for Some Common Particularly Hazardous Substances <ol> <li>(1) Acrylonitrile (CH<sub>3</sub>CN)</li> <li>(2) Bergame (CH)</li> </ol> </li> </ul>	Page 59 59 59 59 60 60 60 60 61 61
	<ul> <li>(2) Benzene (C<sub>6</sub>n<sub>6</sub>)</li> <li>(3) Bis(chloromethyl)ether (BCME), Chloromethyl Methyl Ether, and Other Chloromethyl Ether Derivatives</li> <li>(4) Carbon Monoxide (CO)</li> <li>(5) Carbon Tetrachloride (CCl<sub>4</sub>)</li> <li>(6) Chlorine (Cl<sub>2</sub>)</li> <li>(7) Chloroform (CHCl<sub>3</sub>)</li> <li>(8) Dimethyl Sulfate (DMS) and Diethyl Sulfate (DS)</li> <li>(9) Ethylene Dibromide (l,2-Dibromoethane, EDB)</li> <li>(10) Hydraging (H-NNH-)</li> </ul>	61 62 62 62 63 63 63 64
	<ul> <li>(10) Hydrazine (H<sub>2</sub>NNH<sub>2</sub>)</li> <li>(11) Hydrogen Bromide (HBr) and Hydrogen Chloride (HCl)</li> <li>(12) Hydrogen Cyanide (HCN)</li> <li>(13) Hydrofluoric Acid (HF)</li> <li>(14) Hydrogen Sulfide (H<sub>2</sub>S)</li> <li>(15) Mercury (Hg)</li> <li>(16) Metal aerthemud comment de (including nickel aerthemud (Ni(CO))) iron certhemul</li> </ul>	64 65 65 66 67
	<ul> <li>(16) Metal carbonyl compounds (including nicker carbonyl (NI(CO)<sub>4</sub>), iron carbonyl (Fe(CO)<sub>5</sub>), and osmium carbonyl (Os(CO)<sub>12</sub>)</li> <li>(17) Nitrogen Dioxide (NO<sub>2</sub>)</li> <li>(18) N-Nitrosodialkylamines and Certain Other N-Nitroso Compounds</li> <li>(19) Phosgene (COCl<sub>2</sub>)</li> <li>(20) Selenium (Se) and its compounds</li> <li>(21) Sodium Cyanide (NaCN) and other cyanide salts</li> </ul>	67 68 69 69 69
VIII.	Prior Approval Requirements	71
IX.	Medical Surveillance	72
X.	Accidents and Emergencies	73
	<ul> <li>A. Emergency Procedures</li> <li>B. Medical and First Aid Information</li> <li>C. Laboratory Emergency Information Signs</li> <li>D. Accident Reports</li> <li>E. Accident Report Form</li> </ul>	73 73 73 74 74
XI.	Glossary of terms and symbols	75
XII.	References	77
XIII.	OSHA Lab Standard 29 CFR 1910.1450	80

# Notes

# Part I.

# Information Sheets, General Guidelines, and Forms

# **EMERGENCY PHONE NUMBERS FOR UNIVERSITY SERVICES**

**Campus Police** 24-hour emergency line, 777-9111 (or 7-9111 from a campus phone). This is the number to call for all emergencies (fire, explosion, chemical exposure, ambulance service, *etc.*).

# Call 7-9111 from a campus phone for all emergencies

Health & Safety Programs Unit, 777-5269 during working hours from 8:30 am to 4:30 p.m.

Occupational Health Services (OHS) can be reached at 777-3472 or 777-9057, 8:30 am to 4:30 p.m.

**Thomson Student Health Services** can be reached at 777-3174 during school session and hours of operation from 8:00 am to 5:00 p.m., except for summer session and breaks when hours of operation are 8:30 am to 5:00 p.m.

Employees may be referred to ambulatory care services by appointment at **Richland Memorial Hospital** (phone 765-6448, hours 8:00 a.m. to 4:30 p.m., 5 days a week). For emergency treatment and/or when this facility is closed, employees are to be taken to **Richland Memorial Hospital Emergency Room**, phone 765-7561. **Richland Memorial Hospital Trauma Center** has the expertise for treating chemical illness and injuries and employees are to go directly to this facility for this type of problem.

**Palmetto Poison Center** (at USC College of Pharmacy, <u>http://poison.sc.edu/</u>), phone 1-800-222-1222. **Poison Control Center**, Richland Memorial Hospital (24 hours a day, 7 days a week, phone 765-7359) can deal with emergencies and provide information involving poisons.

When reporting an accident involving a hazardous chemical the following information should be provided:

- (a) the identity of the hazardous chemical(s) to which the employee may have been exposed, preferably in the form of a material safety data sheet (MSDS)(see Part IV.C);
- (b) a description of the conditions under which the exposure occurred; and
- (b) a description of the signs and symptoms the employee is exposure occurred, and
- (c) a description of the signs and symptoms the employee is experiencing.

MSDS databases are available on the Internet. See Part IV.C for more information. All safety-related incidents involving students or employees should be reported to the **Department of Chemistry & Biochemistry** offices (room 113, Graduate Science & Research Center, phone 777-5264). Emergency phone numbers for Departmental personnel include:

John H. Dawson, Professor (Chair, GSRC 113B, Department of Chemistry & Biochemistry, phone 777-5264) Dr. Stephen L. Morgan (Chair, Chemistry & Biochemistry Safety Committee, GSRC 208, phone 777-2461) Dr. Scott R. Goode (GSRC Facilities Manager, GSRC 207, phone 777-2601) Dr. Michael D. Dukes (Assistant Chair, GSRC 113E, phone 777-2687)

Mr. Sam Burgess (Business Manager, GSRC 113B, phone 777-5010)

# **GUIDELINES FOR CHEMICAL SAFETY AND SECURITY**

- 1. All laboratories must have a copy of an up-to-date Chemical Hygiene Plan (CHP). Adjoining labs having a common supervising faculty member can use a common CHP. All lab employees must know the location and content of the CHP; all employees must sign the clearance form in the CHP. The supervisor of each laboratory is responsible for modifying the CHP to include safety and handling procedures specific to the operations conducted in that laboratory.
- 2. Laboratories must have a posted chemical hazard information sign posted on the hallway door to the laboratory. This notice should indicate the major chemical hazards contained in the laboratory, the location of the chemical inventory, and should provide emergency contact information to be used in the event of an emergency.
- 3. All laboratories must possess a chemical inventory itemizing chemical materials present in the laboratory. The location of this inventory should be noted on the chemical hazard information sign for the laboratory. All laboratories should maintain access to material safety data sheets (MSDS) for all chemicals used.
- 4. For personal safety and to insure security for chemical storage and equipment, all exterior doors to laboratory and offices should be locked at all times. Never leave the doors to unattended labs or offices open or unlocked. All areas containing hazardous material storage must be locked.
- 5. Visitors without key access must be escorted at all times in laboratories and offices. Delivery, maintenance, and cleaning personnel must carry visible identification at all times.
- 6. All chemical materials present in laboratories should be correctly labeled and stored appropriately following the recommendations in the CHP. Regulated materials should be maintained in secure areas.
- 7. Do not work alone in the laboratory if the procedures being conducted are potentially hazardous.

# CHEMICAL HYGIENE CLEARANCE FORM

This form (along with any extra pages) should be filed in your copy of the Chemical Hygiene Plan in your laboratory.

Building:     Principle Investigator:     Group Safety Officer:	Room number:
<i>Emergency contacts:</i> Name:	Phone number:

Acknowledgment:

The undersigned agree to the following statements:

Chemical hygiene procedures have been discussed with the workers listed below. We certify that they have attended a regularly scheduled Departmental safety training session, or have taken USC EHS Laboratory safety training courses (see <u>http://ehs.sc.edu/EHSLabMatrix.htm</u> for more information)., and are familiar with the hazards associated with the chemicals in use in our laboratory.

Title:	Name:	Signature:	Date:
Principle Investigator:			
Group Safety Officer:			

I have read and understand the contents of this Chemical Hygiene Plan, and I am familiar with the hazards associated with the chemicals in use in my work area. I hereby acknowledge that I will comply with the prudent practices as described in the USC Department of Chemistry & Biochemistry Chemical Hygiene Plan.

Name:	Signature:	Date:
1		
3.		
4.		
5		
6		
7		
8.		
9.		
10.		

Insert additional copies of this page as needed.

# LABORATORY CHECKLIST

Each laboratory has its own unique procedures, chemicals, and requirements. As necessary, each laboratory supervisor should add sections to the Chemical Hygiene Plan containing additional information specific to the requirements of the individual laboratory.

Section	<u>Title</u>	Date completed
	Chemical Inventory	
	Additional toxic or reactive chemicals in use in this laboratory	
	Emergency and contingency plan associated with above additional chemicals	
	Special personal protection equipment in addition to that specified in the Chemical Hygiene Plan	
	Additional safety references	
	Documentation of training	
	Documentation of Safety Training of all incoming gr is filed at the department safety training web page at URL: <u>http://www.chem.sc.edu/faculty/morgan/safety</u>	aduate students and <u>//safetytrain.html</u>

# ACCIDENT/INCIDENT REPORT FORM

(use additional sheets for more space)

 DATE OF INCIDENT:
 (month) / \_\_\_\_(day) / \_\_\_\_(year)
 Time: \_\_\_\_\_(hr) : \_\_\_\_(min)
 AM
 PM

LOCATION (Building and room number):

**BRIEF DESCRIPTION OF INCIDENT:** 

**POTENTIAL/SEVERITY** (rate low, medium, high):

## DESCRIPTION OF ACCIDENT/INCIDENT INCLUDING BASIC CAUSE:

# **RECOMMENDATIONS FOR PREVENTION OF SIMILAR INCIDENTS:**

Submitted by:	Employee(s) Date:
	Supervisor Date:
Reviewed by:	Chemical Date:
	Hygiene Officer
	Other Date:

# **Part II. Introduction**

# A. Policy

It is the policy of the University of South Carolina to provide a safe and healthy workplace in compliance with the Occupational Safety and Health Act of 1970 and regulations of the Department of Labor including 29 CFR 1910.1450, "Occupational Exposure to Hazardous Chemicals in Laboratories." The full Laboratory Standard (OSHA LAB STANDARD 29 CFR 1910.1450) is included in Part XIII of this Chemical Hygiene Plan.

The University of South Carolina is committed to providing a safe working environment, and believes employees have a right to know about associated health hazards. So employees can make knowledgeable decisions about any personal risks, this Chemical Hygiene Plan (CHP) includes policies, procedures, and responsibilities designed to develop employee awareness of potentially hazardous chemicals in the work place. It is designed as a tool to coordinate safety procedures and to promote employee training in safe work practices. Prudent practice by employees will also set an example for safe work practices by students and visitors.

It is important that employers assume responsibility for laboratory safety. It is also equally important that employees be concerned about their own safety. All employees will have access to pertinent safety information through their supervisory staff. People who work in the laboratory are best able to detect potential hazards in the facility or work procedures. When safety concerns arise, employees are encouraged to contact their supervisor.

A training program has been designed for the benefit and protection of all laboratory employees. Necessary information will be available to inform employees how best to handle hazardous chemicals and how to make use of the new law.

## **B.** Purpose

This document constitutes the Chemical Hygiene Plan required by the above regulation. The purpose of the CHP is to describe prudent practices, procedures, equipment and facilities to be followed by employees, students, visitors, and other personnel working in each laboratory of the Department to protect them from potential health hazards presented by chemicals used in the workplace, and to keep exposures to hazardous chemicals below permissible exposure limits. It is the responsibility of the faculty, administration, and research and supervisory personnel to know and to follow the provisions of this Plan. This plan shall be available in all laboratories for employee review and reference.

# C. Personnel Covered by this Plan

This Chemical Hygiene Plan applies to all work involving hazardous substances that is conducted in space assigned to the Department of Chemistry & Biochemistry. Visitors and individuals holding appointments in other USC departments who plan to conduct research involving hazardous substances in laboratories of the Department of Chemistry & Biochemistry must undergo the chemical hygiene training outlined in Part IV.A and file the Chemical Hygiene Clearance Form (page 6) with your laboratory copy of this Chemical Hygiene Plan before beginning work.

### D. Acknowledgment

This Chemical Hygiene Plan was prepared by Professor Stephen L. Morgan (Department Chemistry & Biochemistry, University of South Carolina, Columbia, SC 29208, email: morgansl@mailbox.sc.edu: phone (803) 777-2461). Portions of this Chemical Hygiene Plan were drawn from the manual: "*Prudent Practices for Handling Hazardous Chemicals in Laboratories*," prepared by the National Academy of Sciences' Committee on Hazardous Substances in the Laboratory (National Academy Press, Washington, D.C., 1981). Substantial portions of this document originated with the Chemical Hygiene Plan prepared by Professor Rick L. Danheiser for the Department of Chemistry at the Massachusetts Institute of Technology. The assistance of Dr. John Baynes, Dr. Robert Bly, Dr. Elizabeth Griffith, Patty Gillies, Dr. Edward Oswald, Dr. Edward Shmunes, and Rae Wharton is also acknowledged.

# Part III. Responsibility, Authority, and Resources

Compliance with applicable laws and implementation of this CHP is the responsibility of the University of South Carolina. The degree of compliance depends directly on administrative emphasis. Success depends on definitive safety objectives and requirements. Employees must understand these objectives and practice the expected safe techniques. If everyone involved in the process *knows of* and *abides by* safety expectations, we are more likely to perform our jobs at a level of safety that is acceptable to all.

Responsibility for chemical hygiene and safety is shared by administrators, the Departmental Safety Committee, laboratory supervisors,

### A. Department Chair

The Department Chair has the responsibility and the authority, with the assistance of other University administrators, to establish and support a safe and healthful laboratory work environment by ensuring resources for the safe laboratory use of chemicals. It is also the Department Chair's responsibility to see that the Chemical Hygiene Plan is written, updated, and implemented. In addition, the Department Chair appoints the Safety Committee and Chemical Hygiene Officer in accordance with the definition provided in paragraph (b) of 29 CFR 1910.1450 and the requirements outlined in this section. The Department Chair has the final responsibility for the safety and health of the employees, visitors, students, and other personnel conducting work in the Department.

### **B.** Safety Committee and Chemical Hygiene Officer

The Safety Committee assists the Chair with the development and implementation of the Department's Chemical Hygiene Plan (CHP). The Safety Committee provides advice and assistance to laboratory supervisors with regard to the training of the Department Chemistry & Biochemistry personnel and the implementation of the CHP. The Safety Committee is chaired by the Department's Chemical Hygiene Officer (CHO). It is the responsibility of the Chemical Hygiene Officer to implement and manage the Chemical Hygiene Plan. The CHO must also work with the Department and University administration to remain current on new regulations, legal requirements, and proposed standards from regulatory agencies. It is the CHO's responsibility to seek ways to improve the Chemical Hygiene Plan, to minimize hazardous waste, and to improve the safety of laboratory operations and procedures through an annual review of the Chemical Hygiene Plan.

### C. Laboratory Supervisors

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

IT Shop—	Mr. J. D. Ham (GSRC 108L, 777-3160)
Mass Spectrometry Laboratory—	Dr. Michael D. Walla (GSRC 108,: 777-2039)
	Dr. Bill Cotham (GSRC 108M,: 777-2039)
Nuclear Magnetic Resonance Laboratory—	Dr. Perry J. Pellechia (GSRC 108K, 777-2088)
	Dr. Helga Cohen (GSRC 108J,: 777-2088)
Stockroom, Department of Chemistry & Biochemistry—	Ms. Jan Miron (GSRC 109,: 777-2396)
Undergraduate Laboratories—	Dr. Lori Amato Knopp (PSC 117, 777-1540)
	Dr. Danny Freeman (PSC 316, 777-8899)
	Dr. William E. Brewer (PSC 312, 777-0458)
	Dr. George Handy (PSC 218A/213, 777-5188)
X-Ray Laboratory—	Dr. Lucasz Lebioda (GSRC 330,: 777-2140)

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

- 1. Seek ways to improve the Chemical Hygiene Plan, to minimize hazardous waste, and to improve the safety of laboratory operations and procedures. Periodically review the CHP and suggest appropriate revisions.
- 2. Instruct all personnel to conduct work in accordance with the Department's Chemical Hygiene plan. Make copies of the approved safety plan and Chemical Hygiene Plan available to the laboratory and support staff.
- 3. Ensure that all staff receives instructions and training in safe work practices, in pertinent aspects of applicable regulations, in use of personal protective equipment, and in procedures for dealing with accidents involving toxic substances.
- 4. Define hazardous operations, designating safe practices and specifying protective equipment.
- 5. Review and approve standard operating procedures for work involving hazardous substances.
- 6. Define the location of designated areas for work with particularly hazardous substances (see Part VII.B) and ensure that an inventory of these substances is properly maintained.
- 7. Direct all personnel to obtain protective equipment necessary for the safe performance of their job. Employees in identified areas of potential risk, and/or those with exposures requiring medical surveillance are to be referred to Occupational Health Services.
- 8. Formulate procedures for dealing with accidents to avoid unexpected exposure of personnel or the environment to toxic substances.
- 9. Take action to correct work practices and conditions that may result in the release of toxic chemicals.
- 10. Instruct laboratory personnel to properly dispose of unwanted and/or hazardous chemicals and materials.
- 11. Arrange for non-laboratory personnel (*e.g.*, contractors and support personnel) to be informed of potential hazards they may be exposed to when working in your laboratory, and provide proper instruction to minimize the risk of harmful exposure to hazardous substances.
- 12. Monitor the safety performance of personnel with regard to required safety practices and techniques.

- 13. When required, arrange for workplace air samples, swipes, or other tests to determine the amount and nature of airborne and/or surface contamination, inform employees of the results, and use data to aid in the evaluation and maintenance of appropriate laboratory conditions.
- 14. Conduct formal laboratory inspections regularly to monitor compliance with existing laboratory procedures and regulations.
- 15. Assist the personnel from the USC Health & Safety Programs Unit when necessary.
- 16. Investigate accidents and report to the Chemical Hygiene Officer incidents that cause (1) personnel to be seriously exposed to hazardous chemicals or materials, or that (2) constitute a danger of environmental contamination (see Part X.E for a copy of the Accident/incident Report Form). Institute procedures that will minimize the repetition of accidents.
- 17. Complete and maintain a chemical inventory of each laboratory under supervision. The form of this inventory is optional at the discretion of the supervisor but computerized inventories should be done wherever possible. MSDSs should be available for every hazardous chemical on the CD-ROM system in the Mass Spectrometry Laboratory or on the Health & Safety BBS (see Part IV.C for more information on accessing these systems).

#### **D.** Group Safety Officers

It is the responsibility of faculty members to appoint a Group Safety Officer for their research laboratory. Group Safety Officers are responsible for evaluating and making recommendations on safety issues that concern their laboratory and the entire Department. Safety Officers also participate in periodic safety inspections of Department laboratories.

Group Safety Officers advise and assist their laboratory supervisors in training new personnel, disseminating safety information, conducting inspections of their group's laboratories, and inspecting and ensuring the maintenance of group safety equipment such as spill control kits, fire extinguishers, safety showers, and eyewash facilities. The Group Safety Officer's responsibilities include, but are not limited to, safety issues involving chemical hygiene. It is recommended that Group Safety Officer be the individual responsible for keeping an accurate record of the amount of highly toxic substances being stored, used, dates of use, and names of persons using the substance. The Group Safety Officer is responsible for filing an accident/incident report form following a laboratory incident resulting in injury or illness, when a near miss incident that might have been more serious occurs, whenever an accident involving fire with flame occurs, and after all releases or spills of potentially hazardous substances. See Part X.E for a copy of the Accident/Incident Report Form.

#### E. Employees, Staff and Research Personnel

Employees are those staff under the direction of the Supervisor. Employees not under the direction of the Supervisor, but who are in an area under the direction of the Supervisor, are also subject to the Department of Chemistry & Biochemistry Chemical Hygiene Plan and the standard operating procedures in effect in that area. Also subject to the plan are all "non-employee" personnel including graduate and undergraduate students, postdoctoral associates, and visiting scientists.

It is the responsibility of employees and other research personnel to follow the procedures outlined in the USC Department of Chemistry & Biochemistry Chemical Hygiene Plan and all standard operating procedures developed under that plan. These include the following:

1. Understand and follow all standard operating procedures and training received.

2. Develop good personal chemical hygiene habits by ensuring that required safety precautions are in place before work is started, by reporting any unrecognized hazardous, and by attempting to minimize the generation of chemical wastes.

3. Understand the function and proper use of all required personal protective equipment. Wear personal protective equipment when mandated or necessary.

4. Report, in writing to your supervisor, any significant problems arising from the implementation of the standard operating procedures.

5. Report to your supervisor and the Department Chemical Hygiene Officer all facts pertaining to every accident that results in exposure to toxic chemicals, and any action or condition that may exist that could result in an accident. Complete an accident/incident report form whenever a laboratory incident results in injury or illness, when a near miss incident that might have been more serious occurs, whenever an accident involving fire with flame occurs, and after all releases or spills of potentially hazardous substances. See Part X.E for a copy of the Accident/Incident Report Form.

6. Contact your supervisor, the Chemical Hygiene Officer, Occupational Health Services, or the Health & Safety Programs Unit if any of the above procedures are not clearly understood.

#### F. College of Arts and Sciences Science Stockroom

The web site at URL: <u>http://www.chem.sc.edu/support/stockroom</u> provides information about the organization and policies of the College of Arts and Sciences Science Stockroom.

#### G. Health & Safety Programs Unit, Occupational Health Services, and Thomson Student Health Center

The services of the Health & Safety Programs Unit are available both in emergency situations and on request in an advisory capacity. **Dial Campus Police at 777-9111 for assistance in any Emergency outside normal working hours.** 

The **Health & Safety Programs Unit** can be reached at 777-5269 during working hours from 8:30 am to 4:30 p.m. The Health & Safety Programs Unit is the component of the University charged with responsibility for control, review, monitoring and advice with respect to exposure to chemical, radiological, and biological agents used in research and teaching. The Health & Safety Programs Unit is charged with responsibility for oversight and control of physical hazards in the workplace. including fire protection, electrical and other safety hazards, and chemical waste disposal arising from work at the University. Subunits within the Health & Safety Programs Unit include the Radiation Safety Unit, the Environmental Health & Safety Unit, The Occupational & Environmental Health Unit, and the Office of the Director. The Health & Safety Programs Unit and/or Occupational Health Services have the responsibility of advising whether, in their judgment, any activity is hazardous to life or health. Based on such recommendations, the USC administration (President, Dean, Department Chair, Principal Investigator, *etc.*) has the authority to stop any activity judged hazardous to life and health. In addition, the Health & Safety Programs Unit has regulatory authority as part of USC's license to use radioactive materials from the Nuclear Regulatory Agency. Apart from these conditions, both the Health & Safety Programs Unit and EMS act in an advisory capacity to the individual Departments to help them provide a safe and healthful workplace.

The Health & Safety Programs Unit and the Occupational Health Services have professional staff that can be called upon for assistance and direction on safety and environmental health problems. The Health & Safety Programs Unit evaluates and implements safety policies and reviews new and existing equipment and operating practices to minimize hazards to the University community and visitors from physical, chemical, biological agents, fire, electricity, explosion, high or low pressure systems, and machinery. The Health & Safety Programs Unit conducts accident investigations, and suggests remedial measures and procedures. It also publishes a safety newsletter. In addition, a waste chemical service picks up potentially hazardous chemicals. Training and assistance in conducting special illness/accident prevention programs are available as required, or as indicated.

**Occupational Health Services (OHS)** can be reached at 777-3472, 777-9057, or 777-0761, 8:30 am to 4:30 p.m. OHS is directed by a board certified occupational health specialist, and staffed with an Occupational Health Nurse. A faculty physician provides consultation in occupational/environmental medicine. All members of the University community should feel free to consult with Occupational Health Services if there are health and safety concerns involving potential chemical, physical, or biological hazards in the workplace.

**Thomson Student Health Services** can be reached at 777-3174 during school session and hours of operation from 8 am to 5 p.m., except for summer session and breaks when hours of operation are 8:30 am to 5:00 p.m.

# Part IV. Information and Training

#### A. Initial Training

All members of the Department of Chemistry & Biochemistry should be familiar with the hazards associated with chemicals present in their work area. Researchers whose work involves use of hazardous substances must be informed as to the proper handling procedures and measures they must take to protect themselves from these hazards. All new personnel in the Department of Chemistry & Biochemistry must complete the following steps prior to beginning work in areas where hazardous chemicals are in use.

1. New personnel must read and understand the **Department of Chemistry & Biochemistry Safety Manual and Chemical Hygiene Plan** and must study any materials provided by their supervisor concerning the **hazardous substances in use in their laboratory**. Each member of the Department must submit a signed copy of the **Chemical Hygiene Clearance Form** to be placed in each laboratories copy of the Chemical Hygiene Plan *prior to beginning work* in areas where hazardous substances are in use. The acknowledgment section of the Chemical Hygiene Clearance Form that states "I *have read and understand the contents of this Chemical Hygiene Plan, and I am familiar with the hazards associated with the chemicals in use in my work area. I hereby acknowledge that I will comply with the prudent practices as described in the USC Department of Chemistry & Biochemistry Chemical Hygiene Plan.*" must be signed by the researcher. The section of the form which states "*Chemical hygiene procedures have been discussed with the workers listed below and we certify that they are familiar with the hazards associated with the chemicals in use in our laboratory* supervisor and Group Safety Officer. In the case of personnel whose work will not involve exposure to hazardous substances, the laboratory supervisor should sign the statement "\_\_\_\_\_\_\_\_ is a member of my group and will not be working in an area in which hazardous substances are in use."

**New graduate students** are required to submit their Chemical Hygiene Clearance Form (page 6) before commencing work in any research laboratory. **Other research personnel** (including postdoctoral fellows, visiting scientists, technicians, and undergraduate students) must submit their Chemical Hygiene Clearance Form within two weeks of the beginning of their appointment. Completed forms will be kept on file in the office of the Department Assistant Chair. In the event that a completed form is not submitted on time as required above, then the worker and their supervisor will be notified in writing by the Department that the individual is not authorized to work in areas where hazardous substances are in use.

2. All personnel whose work will involve the use of hazardous substances are required to attend one of the **Chemical Hygiene Lectures** presented at the start of each academic semester (*e.g.*, August and January); sessions may also be scheduled in June. New personnel are required to attend the next lecture presented after the date of their initial appointment. For personnel whose starting employment date is not compatible with this training schedule, their supervisor is responsible for seeing that all necessary training discussed in this Chemical Hygiene Plan and any training specific to their laboratory is properly conducted and documented. Specifically, individuals not able to attend one of the scheduled safety sessions are required to take the **on-line laboratory safety course** (available at URL: <a href="http://ehs.sc.edu/modules/lab/lab\_intro.htm">http://ehs.sc.edu/modules/lab/lab\_intro.htm</a>). After completion of the entire course, a post-test is presented. After completion of the test, a copy of the score should be printed and submitted to the Chair of the Departmental Safety Committee (Dr. Morgan). Attendance and on-line test records will be maintained in the office of the Department Assistant Chair.

OSHA requires the Chemical Hygiene Training Program to include:

- (1) The existence, location and availability of this CHP document.
- (2) The content of the lab standard 29 CFR 1910.1450 and its appendices (see Part XIII).
- (3) The criteria to select, use and the limitations of personal protective equipment.
- (4) Exposure limits including TLVs and PELs.
- (5) The emergency procedures and the location of the equipment.
- (6) The location of available reference materials including the MSDSs.
- (7) Identification of hazardous chemicals.

Laboratory hazards vary widely from group to group, and consequently it is the responsibility of the **laboratory supervisor** to provide personnel working in their groups with proper information and training on hazardous chemicals. This information does not need to be presented via a formal training session. Information can be from informal group or individual discussions with one's supervisor, posted notices, or handout booklets. Specific training for individual laboratories should include:

(1) Location of the CHP and the chemical inventory.

(2) Labeling information.

(3) Procedures for handling hazardous chemicals including: work practices; proper moving, storing, and use; PELs for specific chemicals used by employee; visual appearance of chemicals used by the employee; environmental monitoring required; signs and symptoms of exposure.

(4) Protective equipment used to prevent over exposure.

(5) Environmental protection including emergency procedures, spill containment methods, and medical consultation procedures.

Some personnel are also required to participate in certain safety seminars and training programs involving blood borne pathogens, respirator use, radiation or laser protection. **Graduate teaching assistants and work-study employees** are also required to attend the Chemical Hygiene Lectures presented once each year at the start of each academic year (usually in August or September).

#### **B. Hazard Identification**

*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 Thomas Cooper Library, and the Health & Safety Programs Unit. Material Safety Data Sheets (see below) are another valuable source of information. Additional information on hazardous chemicals can be obtained by contacting the USC Health & Safety Programs Unit (777-5269). Information on hazardous chemicals is available in the following references:

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

Handbook of Laboratory Safety (3rd ed.), A. K. Furr, Ed., 1989 (704 page reference on all aspects of lab safety).

*Prudent Practices for Handling Hazardous Chemicals in Laboratories,* prepared by the National Research Council, National Academy Press, Washington, D.C., 1981 (available from the National Academy Press, 2101 Constitution Ave., N.W., Washington, D.C. 20418, 291 pages).

*Chemical Hazards of the Workplace* (2nd ed.), N. H. Proctor, J. P. Hughes, and M. L. Fischman, 1988. (573 pages; includes fairly detailed discussions of the toxicology of 438 hazardous substances).

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

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

*Prudent Practices for Disposal of Chemicals from Laboratories,* prepared by the National Research Council, National Academy Press, Washington, D.C., 1983 (available from the National Academy Press, 2101 Constitution Ave., N.W., Washington, D.C. 20418; 282 pages).

*Rapid Guide to Hazardous Chemicals in the Workplace* (2nd ed.), R. J. Lewis, Ed., 1990 (concise compilation of properties and safety data such as PELs, TLVs, *etc.* for 800 substances).

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

Additionally, the USC Health & Safety Programs Unit **web site** (<u>http://ehs.sc.edu/</u>) is used to disseminate information on health and safety issues. This web site provides a wealth of safety-related information including the following:

#### Our Program: Policies, Manuals, Safety Training:

- President Palms' Memo to USC Faculty and Staff (<u>http://ehs.sc.edu/palms.htm</u>)
- About EHS: Mission, Responsibilities and Staff Info (<u>http://ehs.sc.edu/dept.htm</u>)
- ONLINE USC Safety Program Guide (<u>http://ehs.sc.edu/guides/toc.htm</u>)
- ONLINE Radiation Safety Manual (<u>http://ehs.sc.edu/rsm/manualpage.htm</u>)
- List of Departmental Safety Managers (<u>http://ehs.sc.edu/Departmental%20Safety%20Managers.htm</u>)
- Safety Training Page (<u>http://ehs.sc.edu/training/safety\_training.htm</u>)
- On-line Safety Training Modules (<u>http://ehs.sc.edu/training/online\_list.htm</u>)
- Downloadable Forms Chemical Hygiene Plan, Radiation Safety forms, self-audit checklists (<u>http://ehs.sc.edu/forms.htm</u>)

### Safety Information and Resources:

- Laboratory Safety Information and Resources (<u>http://ehs.sc.edu/laboratory.htm</u>)
- Fire Safety Information (<u>http://ehs.sc.edu/fireinfo/fire.html</u>)
- MSDS Searches (<u>http://ehs.sc.edu/msds.htm</u>)
- Severe Weather Safety Guide from NOAA <u>http://www.nssl.noaa.gov/nws/safety.html#winter</u>)
- Other Safety and Health Information Resources (<u>http://ehs.sc.edu/links.htm</u>)

The Laboratory Safety Information page (<u>http://ehs.sc.edu/laboratory.htm</u>) contains links to:

- Downloadable copy of this Chemical Hygiene Plan in MS Word 6.0 format (also available in Wordperfect 6.0 format).
- The OSHA Laboratory Standard regulatory text from the OSHA website (<u>http://www.osha-slc.gov/OshStd\_data/1910\_1450.html</u>).
- Laboratory Safety On-line training designed by the Howard Hughes Medical Institute (<u>http://ehs.sc.edu/modules/lab/lab\_intro.htm</u>). Note that a web browser must be set to accept cookies for this course.
- Laboratory Standard section of the USC Safety Program Guide (<u>http://ehs.sc.edu/guides/lab\_gui.htm</u>). This is the section of the USC Safety Program Guide that deals with Laboratory Safety.
- A self-audit checklist for laboratories (<u>http://ehs.sc.edu/guides/lab\_gui.htm</u>).
- MSDS Searches (<u>http://ehs.sc.edu/msds.htm</u>). Need an MSDS for a particular chemical? Get it here from one of several searchable databases.
- Glove Selection Chart (<u>http://ehs.sc.edu/gloves.htm</u>). Confused about which type of glove is appropriate for the chemical you're using? Consult this chart to select the proper glove.
- Chemical Storage Guidelines (<u>http://ehs.sc.edu/chemstorage.html</u>). Do you have questions about how to store chemicals in your lab? Look at this page for guidance.

Call Patty Gillies at the Health & Safety Programs Unit (777-5269) to ask questions.

It is a good idea to learn to use the web to access safety information on substances with which you will be working before starting a research project. It is *not* a good idea to have to learn the use of these systems during an emergency while a coworker is being transported to the hospital following a laboratory accident.

## C. Container Labeling

In laboratories the primary means of ensuring general hazard identification and recognition of specific chemical hazards is through sound container labeling practices. It is very important to implement consistent labeling practicing that all affected employees understand. To achieve this goal, container labeling shall follow the rules below:

- 1. Container labeling.
  - a. *Original container labels*. Original containers of chemicals as purchased from the supplier or manufacturer contain the following labeling information:
    - i. Chemical identity of product name.
    - ii. Appropriate hazard warnings (e.g., symbols, statements, NFPA label providing health, flammability, reactivity, *etc.*).
    - iii. Name and address of chemical manufacturer or responsible party.
    - iv. Often, labels will include supplementary safety information including a written description of hazards, first aid, and disposal guidelines.

Original container labels must be protected so that the identity of the contents and the hazards those contents present are known. All laboratory workers will ensure that original container labels are legible, not removed, or defaced *unless the container is emptied of all original contents and rinsed out*.

- b. *Secondary* container labels. If a chemical is freshly prepared in the laboratory or is to be stored in a container other than the manufacturer's bottle, the following information should be on the container:
  - i. Chemical identity of product name.
  - ii. Concentration or approximate purity (e.g., molarity, normality, percent, etc.).
  - iii. Date of formulation.
  - iv. Name of user.
  - v. If the chemical is determined to be hazardous, a hazard warning (*e.g.*, health, flammability, reactivity, *etc.*).
- 2. Hazardous waste labels. Hazardous waste containers shall be labeled with the following information:
  - i. Waste accumulation start date.
  - ii. The words "Hazardous waste."
  - iii. A label or sign identifying the major hazard(s) associated with the waste in the container.

The National Fire Protection Association (NFPA) has designed a system of warning labels that, with both an easy to interpret code and color, convey the major hazards associated with a chemical. The color coded NFPA labels denote a degree of danger through a numerical rating system. The figure and table on the next page summarize the NFPA color and rating schemes.





Hazard rating	Blue (Health)	Red (Flammability)	Yellow (Reactivity)	White (Special notice)
0	No hazard	Material will not burn	Material is stable	OX: Material is an oxidizer
1	Material can cause irritation if not treated	Material will ignite after considerable heating. Flash point is above 200 ° F	Material is normally stable, but is unstable at high temperature and pressure, and reacts with water.	₩: Material is water reactive. Do not contact with water.
2	Material can cause injury. Requires prompt medical treatment.	Material ignites if moderately heated. Flash point above 100 ° F, but below 200 °F.	Material is normally unstable, but will not detonate.	RAD: Material is radioactive. Radiation label is preferred.
3	Material can cause serious injury despite medical treatment.	Material can be ignited under almost all ambient temperatures. Flash point below 100 °F.	Material can explode but requires strong initiating force or heating under confinement,	CAR: Material is a carcinogen. Carcinogen label is preferred.
4	Material can cause death or major injury despite medical treatment.	Very flammable gases or volatile flammable liquids. Flash point below 73 °F.	Material readily explodes at normal temperatures and pressure.	

#### D. Material Safety Data Sheets (MSDS) and Internet Resources

Material Safety Data Sheets describe the hazards of a chemical material and provide information on how the material can be safely handled, used, stored, and disposed. A 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 USC the first time a compound is ordered by an employee. Laboratories should maintain access to material safety data sheets (MSDS) for all chemicals used, either by storing MSDSs received from suppliers or by maintaining access to electronic sources of MSDS information.

The following web sites contain MSDSs and other information on hazardous chemicals. These sites are accessible on the Departmental network connected to the Internet. Web sites can be added as bookmarks in web browsers for ready access. MSDS databases, in particular, are extremely valuable because they provide everyone with easy access to thousands of Material Safety Data Sheets on hazardous compounds. This information can be viewed, printed, or saved to disk from these sources.

#### Web sites for Material Safety Data Sheets

Description	URL
USC Environmental health & Safety web site: A list of resources and laboratory safety information, including information on laboratory inspections, hazardous waste management and MSDS resources.	http://ehs.sc.edu/msds.htm
Agency for Toxic Substances and Disease Registry (Centers for	http://www.atsdr.cdc.gov/atsdrhome.html
Canadian Center for occupational Health (MSDS database and links to other chemical health & safety sites):	http://www.ccohs.ca/
Chemical Abstracts Service (American Chemical Society):	http://info.cas.org/welcome.html
Cornell University safety web site (a MSDS database of 300,000+ compounds):	http://msds.pdc.cornell.edu/issearch/msdssrch.htm
Envirocare, Int. MSDS search:	http://www.msdssearch.com/
Fisher Scientific Internet Catalog (including online MSDS searches):	http://www.Fisher1.com/
Interactive Learning Paradigms, Inc. (this site contains information on MSDSs and lists over 85 different MSDS sites on the Internet):	http://www.ilpi.com/msds/index.html
Vermont SIRI (safety information including three web sites with MSDSs):	http://siri.org/
Vermont SIRI MSDS (Site Two):	http://siri.org/msds/
Chemfinder Database Searching (a service of CambridgeSoft Corporation):	http://www.chemfinder.com/

### E. Chemical Inventory.

An inventory of chemicals on-hand in each laboratory should be maintained and updated as chemical materials are purchased or removed form service. The laboratory supervisor is ultimately responsibility for this inventory, although it is recommended that Group Safety Officers be assigned the responsibility for ensuring that this inventory list is kept up to date. The inventory may be available in written or electronic format. The inventory may be kept in a document or data base file of the user's design.

# Part V. Protective Equipment

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

### A. Eye Protection

To minimize the risk of eye injury, USC policy requires that all personnel, including visitors, wear eye protection at all times while in Department of Chemistry & Biochemistry laboratories. This eye protection policy is necessary in order that the University comply with both South Carolina and Federal law (e.g., Code of Federal Regulations, Title 29, Section 1910.133). Eye protection is required whether or not one is actually performing a "chemical operation", and visitors should not be permitted to enter a lab unless they wear appropriate eye protection. Groups that handle chemicals should provide a supply of safety glasses at the entrance of each laboratory for the use of Physical Plant Services personnel and visitors. Goggles for visitors can also be purchased from the Chemistry Stockroom in GSRC 109.

Safety glasses must meet the American National Standards Institute standard Z87.1-1989 that specifies a minimum lens thickness (3 mm), certain impact resistance requirements, *etc.* 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** also do not provide minimally acceptable protection. 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 (goggles) is therefore required for all workers in the Department of Chemistry & Biochemistry 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. Prudent safety practice and the policy of the Department of Chemistry & Biochemistry prohibit the wearing of contact lenses in chemical laboratories in which chemicals are handled. If a worker's vision requires optical correction, regular spectacles should be worn underneath approved safety goggles at all times. Contact lenses worn by persons working in laboratories can increase injury from chemical splashes because the wearer may not be able to remove the lenses to permit thorough irrigation and a person giving first aid may not know that contact lenses are being worn or how to remove them. Many physicians believe that the substitution of contact lenses for spectacles in industrial workers is contraindicated in workers whose eyes may be exposed to dusts, molten metals, or irritant chemicals. Small foreign bodies, which normally are washed away by tears, sometimes become lodged beneath contact lenses, where they may cause injury to the cornea. Similarly, chemicals splashed into the eye may be trapped under a contact lens and cause extensive corneal damage before the lens can be removed and the eye adequately irrigated. Furthermore, soft lenses can absorb solvent vapors even through face shields and, as a result, adhere to the eye. Since removal of a contact lens for urgent irrigations after injury is made so difficult by spasm of the eyelids, the contact lens wearer is in even greater need of protection than his/her counterpart who does not wear contact lenses, if the job carries high potential risk of eye injury. Contact lenses are not in themselves protective devices and in fact may increase the degree of injury to the eye.

**Goggles provide the minimal level of acceptable protection when working in a chemical laboratory**. Goggles should be worn when carrying out operations in which there is reasonable danger from splashing chemicals, flying particles, *etc.* For example, goggles are required when working with glassware under reduced or elevated pressures (e.g. sealed tube reactions), when handling potentially explosive compounds (particularly during distillations), and when employing glass apparatus in high-temperature operations. In some instances "safety shields" should be set up around experiments for additional protection. Since goggles offer little protection to the face and neck, **full-face shields** should be worn when conducting particularly hazardous laboratory operations. In addition, the use of laser or ultraviolet light sources requires special glasses or goggles that have been approved by the USC Health & Safety Programs Unit (777-5269).

## **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 potentially hazardous chemical should 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 VI and VII, work with certain chemicals and classes of chemicals requires that protective apparel such as a lab coat or chemical-resistant apron be worn.

3. Sandals, bare feet in shoes, or open-toed shoes should be avoided. Long hair and loose clothing should be confined when present in the laboratory. Rules that are more stringent may apply when working with hazardous substances (see Part VI.C.2).

4. Suitable gloves must always be worn when working with hazardous substances. Choose gloves made of material known to be (or tested and found to be) resistant to permeation by the substance in use. 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.* Even silicone grease leaves an undesirable sticky residue behind if a door is opened or a telephone is answered using a grease-contaminated glove.

## C. Respirators

Respiratory hazards should be controlled at their point of generation by using engineering controls and good work practices. In keeping with this goal, the use of respirators as the primary means of protecting employees from airborne hazards is considered acceptable only in very specific situations and only with prior approval from the Departmental Safety Committee and the USC Health & Safety Programs Unit. The routine use of respirators as a means of primary control is strongly discouraged.

Approval may be granted only for such situations as short-time 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 1910.134-135, see Part XIII) 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. Appointments for medical evaluations can be arranged by calling Occupational Health Services at 777-3472. After an examination, the physician will issue a "respirator-user permit". Training and fit testing will be conducted by the Industrial Hygienist prior to the medical evaluation.

3. The type of respirator to be used will be selected in consultation with the USC Health & Safety Programs Unit (777-5269). Respirators can be purchased only after such consultation, and are assigned to individuals for their exclusive use. Personnel must participate in a Respirator Training Program prior to using a respiratory device. This training is provided by qualified personnel specified by the USC Health & Safety Programs Unit (777-5269) and includes discussion of the proper use, maintenance, testing, cleaning, and storage of respiratory equipment.

4. All users must undergo fit testing (conducted by the USC Health & Safety Programs Unit (777-5269)) when a respirator is first issued and subsequently as required by OSHA regulations. The USC Health & Safety Programs Unit (777-5269) will also maintain records of respirator users.

#### **D.** Laboratory Hoods

Local exhaust ventilation is the primary method used to control inhalation exposure, skin exposure, and eye exposure to hazardous substances. The laboratory hood is the most common local exhaust method used in the Department of Chemistry & Biochemistry. Other types of local exhaust include vented enclosures for large pieces of equipment or chemical storage, and snorkel types of exhaust for capturing contaminants near the point of release. Local exhaust systems consist of some type of hood, ductwork, and fan located on the roof. Some systems are equipped with air cleaning devices (HEPA filters or carbon adsorbers). In most cases individual fans service each hood.

*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 all work with "particularly hazardous substances" (see Part VI and VII). 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 duct work (this includes disabling hood alarm systems!) without first calling the Department Business Manager (Mr. Sam Burgess, 777-5010) and the USC Health & Safety Programs Unit (777-5269). Any changes made to the local exhaust system must by approved by the USC Health & Safety Programs Unit (777-5269).

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 separate enclosure specifically designed for large equipment so that the laboratory hood can be used for its intended purpose.

The USC Health & Safety Programs Unit regularly inspects all laboratory hoods. Additionally two staff members in the Department of Chemistry & Biochemistry (Mr. Joel Babbit and Mr. Earl Brooks) have received certified training in hood velocity measurements. 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. It is the responsibility of researchers and laboratory supervisors to notify the Department Chemical Hygiene Officer if any hoods in their laboratory do not have an updated certification label.

If a hood fails inspection due to a problem that Physical Plant Services can correct (*e.g.*, a slipping fan belt, cracked duct work) then the Department Business Manager (Mr. Sam Burgess, 777-5010) will submit a work order to Physical Plant Services to have it repaired. Physical plant will notify the Health & Safety Programs Unit when the repairs have been made, and the fume hood is then re-inspected. If a hood functions poorly due to incorrect use (*e.g.*, cluttered hoods) then USC Health & Safety Programs Unit will notify the Laboratory Supervisor and Department Chemical Hygiene Officer.

The minimum acceptable face velocity criteria used for hoods is 100 feet per minute. During comprehensive 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 average 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 air flow patterns. No back flow that results in the release of smoke from the laboratory hood is permitted. The type of hood and the physical condition should be recorded during inspection. If parts of the hood are missing such as the airfoil or side panels, this will also be noted. Removal of airfoils usually produces a hood with unacceptable containment.

If there is any question about a laboratory hood's operation the USC Health & Safety Programs Unit (777-5269) 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 USC Health & Safety Programs Unit. If any changes of any kind are made to the laboratory hood system, the USC Health & Safety Programs Unit (777-5269) should be notified so that a new hood inspection can be conducted.

The following general rules should be followed when using laboratory hoods:

1. No hoods should be used for work involving hazardous substances unless it has been inspected within the last year.

3. Never put your head inside an operating laboratory hood to check an experiment. The plane of the sash is the barrier between contaminated and uncontaminated air.

3. Always try to keep hazardous chemicals at least six inches behind the plane of the sash.

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. Keep the sash closed when not conducting work in the hood.

5. Avoid cluttering your hood with bottles or equipment. Keep it clean and clear. Only materials actively in use should be in the hood. This will provide optimal containment and reduce the risk of extraneous chemicals being involved in any fire or explosion that may occur in the hood.

6. The hood must remain "ON" at all times when a chemical is inside the hood, regardless whether any work is being done in the hood.

7. Vent ducts and fans must be kept clean and clear of obstructions.

8. Promptly report power failure or any suspected hood malfunctions to the laboratory supervisor, to the Department Business Manager (Mr. Sam Burgess, 777-5010) and, in an emergency, to the USC Health & Safety Programs Unit (777-5269).

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, J. A. Young, Ed., John Wiley, NY, 1987, pp. 287-319.

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

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

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

It is USC policy that personnel are not required to extinguish fires that occur in their work areas. However, as discussed in Part VI.D.3, under reasonable/appropriate circumstances suitably trained personnel may attempt to extinguish fires. All laboratories in the Department of Chemistry & Biochemistry are provided with carbon dioxide extinguishers and generally several other types of extinguishers as well. All fire extinguishers should be mounted on a wall or be standing vertically on the floor in an area free of clutter, normally near the entrance to the laboratory. 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.

Types of fire extinguishers:

<u>Class A extinguishers</u> are for ordinary combustible materials such as paper, wood, cardboard, and most plastics. The numerical rating on these types of extinguishers indicates the amount of water it holds and the amount of fire it can extinguish. Geometric symbol (green triangle)

<u>Class B</u> fires involve flammable or combustible liquids such as gasoline, kerosene, grease and oil. The numerical rating for class B extinguishers indicates the approximate number of square feet of fire it can extinguish. Geometric symbol (red square)

<u>Class C</u> fires involve electrical equipment, such as appliances, wiring, circuit breakers and outlets. Never use water to extinguish class C fires - the risk of electrical shock is far too great! Class C extinguishers do not have a numerical rating. The C classification means the extinguishing agent is non-conductive. Geometric symbol (blue circle)

<u>Class D</u> fire extinguishers are commonly found in a chemical laboratory. They are for fires that involve combustible metals, such as magnesium, titanium, potassium and sodium. These types of extinguishers also have no numerical rating, nor are they given a multi-purpose rating - they are designed for class D fires only. Geometric symbol (Yellow Decagon)

<u>Class K</u> fire extinguishers are for fires that involve cooking oils, trans-fats, or fats in cooking appliances and are typically found in restaurant and cafeteria kitchens. Geometric symbol (black hexagon)

Generally fire extinguishers in the Department of Chemistry & Biochemistry are of the first three types listed.

1. **Halon extinguishers** are effective against all classes of fires except those involving burning metals (class D). As these extinguishers do not leave a residue after use they are the primary extinguishers of choice in any laboratory working with electronic instrumentation. However, Halon extinguishers are more expensive and special purpose extinguishers may be more effective in certain cases. Halon 1301 is a halogenated hydrocarbon, bromotrifluoromethane. Although no residue remains behind, toxic effects when agent concentration exceeds 7% are possible. In the near future, the manufacturer of Halon extinguishers (DuPont) will be replacing Halon with a product that is not a halogenated hydrocarbon.

2. Carbon dioxide extinguishers are effective against Class B fires, (involving burning liquids such as solvents) and Class C electrical fires. They are not as effective against burning paper or trash fires. Do not use a  $C0_2$  extinguisher against fires involving alkali and certain other metals (such as Al, Mg, and Zn) and compounds such as lithium aluminum hydride.

3. **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.

4. **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.

5. **Met-L-X and Met-L-Kyl**. These extinguishers are effective against burning metals including magnesium, lithium, sodium, potassium, reactive metal alloys, metal hydrides, metal alkyls, and other organometallic compounds (Class D fires).

6. 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.

**Fire blankets** located in some laboratories do not meet the require for a suitable fire extinguisher but are useful for extinguishing burning people. Throw the fire blanket over or around a person whose clothes are on fire, make the person lie down on the floor, and roll the person and blanket on the ground to extinguish the fire.

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 USC Health & Safety Programs Unit at 777-5269.

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), see Part XIII). Keep all passageways to the eyewash and shower clear of any obstacle (even a temporarily parked chemical cart). In the event of **a chemical splash affecting the eye(s)**, **immediate flushing with copious amounts of water for up to 20 minutes is crucial.** Medical evaluation should be sought for any/all eye trauma.

It is the responsibility of Group Safety Officers to inspect the portable fire extinguishers, safety showers, and eyewash facilities in their laboratories once each month. Fire extinguishers are also inspected and tagged regularly by the Health & Safety Programs Unit and Physical Plant Services. Safety showers and eyewash facilities are also inspected at least twice a year. The flow through the safety shower should be minimum of 30 gallons per minute.

In addition to the inspections performed by the Health & Safety Programs Unit, the Department of Chemistry & Biochemistry Safety Committee also holds laboratory safety inspections several times each year. These inspections are sometimes unannounced and include the inspection of all safety equipment, such as fire extinguishers, safety showers, and fire blankets.

# Part VI. Standard Operating Procedures for Work with Hazardous Substances

### A. Exposure Guidelines

Most materials have some guidelines for exposure, such as *Threshold Limit Values* (TLV) or *Permissible Exposure Limits* (PEL). When such values exist, they will be used to assist the Chemical Hygiene Officer in determining proper safety precautions, including controls measures and safety apparel.

When TLV or PEL values exist and are low, the user of the chemical must use it in an operating fume hood or glove box. If a fume hood or glove box is not available, a respirator will be used in accordance to the respiratory program (Part V.C).

When TLV or PEL values are not available for a substance, the *Lethal Dosage* that kills 50% of a population of test animals  $(LD_{50})$ , if available, can serve as a guide. If the  $LD_{50}$  is low, then the chemical must also be used in a fume hood. Sometimes the *Lethal Concentration* that kills 50% of a population of test animals by the inhalation route  $(LC_{50})$  is also reported in the scientific literature. The possibility of absorption of a chemical through the skin should always be considered as well.

Whenever a chemical has a high vapor pressure, meaning that it evaporates quickly at room temperature, it must be used in a fume hood. Those controls are necessary even if the chemical with the high vapor pressure also has a very high TLV or  $LD_{50}$ , because such chemicals are likely to reach their exposure limits in air at least as quickly as a chemical with low exposure guidelines and a low vapor pressure.

Fume hoods and/or glove boxes and/or respirators will be used when:

- (1) The TLV or PEL is below 50 ppm or  $100 \text{ mg/m}^3$ ; or
- (2) The  $LD_{50}$  by ingestion is 50 mg/Kg or less; or
- (3)The LD<sub>50</sub> by contact is 200 mg/Kg or less; or
- (4) The  $LC_{50}$  by inhalation is 200 ppm or less, or 2 mg/liter or less, or;
- (5) The vapor pressure is above 50 mm at 20 °C.

#### **B.** 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 Department of Chemistry & Biochemistry 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 become 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 which 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, see Part XIII) 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 VII. Select carcinogens (defined in detail in Part VII.A.1) include compounds for which there is evidence from human studies that exposure can cause cancer. For a large number of other compounds there is limited evidence of carcinogenicity from studies involving experimental animals. These compounds should be handled using the general procedures for work with hazardous substances outlined in Part VI.C below.

It is important to recognize that many of the substances involved in research in Departmental laboratories are new compounds and have not been subjected to testing for carcinogenicity. Researchers should therefore be familiar with the specific classes of compounds and functional group types that have previously been correlated with carcinogenic activity. The following discussion provides an introduction to this subject and lists representative compounds in each class that are *"reasonably anticipated to be carcinogens"* based on animal tests. Always keep in mind that as a general rule, all new and untested compounds should be regarded as being toxic substances.

Classes of Carcinogenic Compounds (\*select carcinogens)

Alkylating agents: α-halo ethers

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

Alkylating agents: sulfonates

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

#### Alkylating agents: electrophilic alkenes and alkynes

\*acrylonitrile acrolein ethyl acrylate

#### Acylating agents

\*β-propiolactone β-butyrolactone dimethylcarbamoyl chloride

Organohalogen compounds

\*1,2-dibromo-3-chloropropane \*mustard gas (bis(2-chloroethyl)sulfide) \*vinyl chloride carbon tetrachloride chloroform 3-chloro 2-methylpropene 1,2-dibromoethane 1,4-dichlorobenzene 1.2-dichloroethane 2,2-dichloroethane 1,3-dichloropropene hexachlorobenzene methyl iodide methylene chloride (1,1-dichloromethane) 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) \**a*-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 *cis*-platin progesterone reserpine safrole

Miscellaneous organic compounds

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

#### Miscellaneous inorganic compounds

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

The preceding compounds were selected from lists of substances identified as carcinogens or potential carcinogens by OSHA, the International Agency for Research on Cancer (IARC), and the Annual Report on Carcinogens published by the National Toxicology Program (NIP). The Health & Safety Programs Unit (777-5269) should be consulted for additional information.

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

#### (2) Reproductive Toxins

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

Information on reproductive toxins can be obtained from Material Safety Data Sheets, by contacting the Health & Safety Programs Unit (777-5269), and by consulting the *Catalog of Teratogenic Agents*, Sixth Edition; T. H. Shepard, Johns Hopkins University Press, Baltimore, 1989. Also see R. E. Beyler, and V. K. Meyers (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.

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	biphenyls
estradiol	toluene
formaldehyde	vinyl chloride
formamide	xylene

Partial List of Reproductive Toxins

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

MSDS databases (see Part IV.C) and the safety library (see Part IV.B) in the Departmental Mass Spectrometry Laboratory may be useful in providing information relevant to this decision.

The period of greatest susceptibility to embryotoxins is the first 8-12 weeks of pregnancy, a period which includes time when a woman may not know she is pregnant. Consequently, women of childbearing potential should take care to avoid significant contact with reproductive toxins. Pregnant women and women intending to become pregnant should consult with their laboratory supervisor and the Occupational Health Services with regard to the type of work they may safely perform and the special precautions they should take. The MSDS databases (see Part IV.C) and the safety library (see Part IV.B) in the Departmental Mass Spectrometry facility may be useful in providing information relevant to this decision.

#### (3) Corrosive Substances

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

#### (4) Irritants

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

#### (5) Toxic and Highly Toxic Agents

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

	Toxic	Highly Toxic
Oral LD <sub>50</sub> (albino rats)	50-500 mg/kg	< 50 mg/kg
Skin Contact LD <sub>50</sub> (albino rabbits)	200-1000 mg/kg	< 200 mg/kg
Inhalation LD50 (albino rats)	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 certain halogenated hydrocarbons);

(c) neurotoxins (substances that produce their primary toxic effects on the nervous system such as mercury, acrylamide, fluorophosphates, and carbon disulfide);

(d) agents which act on the hematopoietic system (such as carbon monoxide and cyanides which decrease hemoglobin function and deprive the body tissues of oxygen), and;

(e) agents, which damage lung tissue such as asbestos and silica.
# (7) Sensitizers

A sensitizer (allergen) is a substance that causes exposed people to develop an allergic reaction in normal tissue after repeated exposure to the substance. Examples of allergens include diazomethane, chromium, nickel, formaldehyde, isocyanates, arylhydrazines, benzylic and allylic halides, and many phenol derivatives. A number of these compounds are also hazardous for other reasons and require special handling because of carcinogenicity, corrosiveness, *etc.*)

#### (8) Flammable and Explosive Substances

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

### C. General Procedures for Working with Toxic Substances

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

**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 Industrial Hygiene Office.

**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).

**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.

**Be prepared for accidents.** Before beginning an experiment, know what specific action you will take in the event of the accidental release of any hazardous substances involved. Know the location of all safety equipment including fire extinguishers, fire blankets, eye washes, safety showers, spill carts and spill control materials, and be familiar with the location of the nearest fire alarm and telephone. Know what telephone numbers to call in the event of an emergency. Emergency phone numbers are listed on page 2 of this Chemical Hygiene Plan which should be copied and posted by every phone. Know the location of the circuit breakers for your laboratory (but do not turn these breakers off/on indiscriminately—loss of power can be hazardous to certain laboratories and harmful to instrumentation).

Assume the worst-case scenario when in doubt with regard to a compound's toxicity. Assume that the level of toxicity for compounds created in the laboratory is at least as toxic as the precursor molecule(s) unless the molecule created has a defined toxicity.

It should be evident from the discussion in Part VI.B that the majority of chemicals in research laboratories must be considered to be "hazardous substances." In addition to the four general principles outlined above, the following procedures should be standard practice for all work involving the use of hazardous substances.

# (1) Eye Protection

USC policy requires that all personnel, including visitors, wear eye protection (goggles) at all times while in Department of Chemistry & Biochemistry laboratories. Eye protection is discussed in detail in Part V.A of this Chemical Hygiene Plan.

# (2) Personal Apparel

Do not wear sandals or open-toed shoes or shoes made of woven material when working with hazardous substances. Confine long hair and loose clothing. Use suitable protective apparel including gloves as discussed in detail in Part V.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 apparel is mandatory; lab coats and personal protective equipment should not be worn outside the laboratory to eating areas.

# (3) Avoid Skin Contact and Ingestion of Hazardous Substances

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

(a) Wear gloves that are not permeable to the hazardous substances being used (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 instead be used to provide vacuum.

(c) Never taste laboratory chemicals.

(d) Wash your hands with soap and water immediately after working with hazardous chemicals and after removing gloves.

(e) Eating, drinking, smoking, gum-chewing, tobacco chewing, applying cosmetics, or inserting/removing contact lenses in laboratories where hazardous substances are in use **is prohibited by Federal law**. Do not store food or beverages or 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 gases or aerosols should be conducted in a laboratory hood or other containment device whenever possible. See Part V.D for a detailed discussion of laboratory hoods. OSHA Permissible Exposure Limits (PELs) and American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Values (TLVs) should be observed when working with hazardous substances for which PELs and TLVs have been established (see *Prudent Practices* pp. 257-276 for a table of TLVs of many common laboratory chemicals). Never smell compounds of unknown toxicity.

# (5) Equipment Maintenance

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

# (6) Housekeeping

Common housekeeping practices contribute greatly towards chemical hygiene and safety. A clean work area is much safer than a cluttered or dirty one. Laboratory staff should also be aware of the needs of custodial activities. The safety of any persons in the laboratory is that laboratory's responsibility. If the laboratory has requested custodial service, that lab must then take on the responsibility of providing save working conditions for these workers.

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 emergency equipment (showers, eyewashes, or fire extinguishers) must not be obstructed.

(c) All gas tanks or cylinders should be secured to walls or benches by appropriate chains or fasteners; cylinder caps should be put on the cylinder when it is not connected to apparatus.

(d) Organic solvents should not be stored on the floor and one-liter (and larger) bottles of solvent must be stored below eye level (*e.g.*, in cabinets).

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

(f) All chemicals should be placed in proper storage areas by the end of each workday. No chemicals are stored in aisles, stairwells, on desks or workbenches, on floors or in hallways, or left on shelves over the workbenches. Keep all work areas and especially workbenches clear of clutter and obstructions.

(g) All chemicals containers should be labeled with both the identity of the chemical and its hazards as discussed in section IV.B.

(h) All spills should be promptly cleaned up and waste properly disposed.

(i) All broken glass should be disposed of in a labeled vessel designed for that purpose. Broken glassware must not be picked up by hand. Instead, it must be collected with tongs or swept up with a dustpan and brush. To minimize aerosol formation, broken glass must not be dropped into a disposal container. Instead, broken glassware should be placed gently into the container.

(j) All needles and other sharp materials should be placed in appropriate "sharps disposal' containers. Do not place such objects in ordinary trash containers because they constitute a hazard to lab personnel and cleaning staff.

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

Researchers should avoid conducting work with hazardous substances when they are alone in the laboratory. When working alone late at night or over long weekend periods, arrange with your laboratory supervisor, laboratory co-workers, workers in other laboratories, or even the Campus Police 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 (see Prior Approval Requirements in Part VIII).

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

#### (8) Children and Pets in Laboratories

Pets such as dogs are not permitted in laboratories where hazardous substances are stored or are in use. Special arrangements may be made for helper dogs, *etc.*, in accordance with the American Disability Act. Except on guided tours, children are only permitted in the Department while under the direct supervision of their parent or other adult and are not permitted in laboratories.

### (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, purchase the minimum quantities of commercial chemicals necessary for your research.

(b) All containers of chemicals should be properly labeled as discussed in section IV.B.. 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) Flammable liquids should be stored in steel storage cabinets with only small quantities kept at workbenches. Quantities greater than 1 liter should be stored in metal or break resistant containers.

(d) Refrigerators used for storage of flammable chemicals must be explosion-proof or laboratory-safe type units. Storage trays or secondary containers should be used to minimize the distribution of material in the event a container should leak or break.

(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 all chemical substances present in their laboratories.

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

#### (10) Transporting Hazardous Substances

USC 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 handle(s), 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. To protect other workers and the environment, a laboratory sink or the sewer system is *not* an appropriate means of disposal.

#### (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 individual researchers (with the assistance of their laboratory supervisor) to evaluate the properties of the excess and waste chemicals resulting from their work, and to determine when special handling procedures are needed outside the general guidelines outlined below. The USC Health & Safety Programs Unit (777-5269) should be consulted for assistance in planning the disposal of such hazardous compounds. Detailed procedures for the laboratory destruction of a number of hazardous chemicals can be found in Chapter 6 of *Prudent Practices for Disposal of Chemicals from Laboratories* and in the reference *Destruction of Hazardous Chemicals in the Laboratory* by G. Lunn and E. B. Sansone.

Disposal of excess and waste chemicals is arranged by calling the USC Health & Safety Programs Unit (777-5269) which will send an employee to pick up and transport the materials to the special storage area maintained by the Health & Safety Programs Unit. The waste chemicals must be prepared for pickup by storing them in **break-resistant containers** (metal, plastic, or plastic-coated glass), or in breakable containers enclosed within "approved **secondary containers**" (*i.e.*, large rubber, metal, or plastic bottle carriers with carrying handles). Large quantities of the same chemical or compatible chemicals must be poured into the carboys provided by the Health & Safety Programs Unit. If there is uncertainty about chemical compatibility, call the Health & Safety Programs Unit (777-5269). Each container must have attached to it a **"Hazardous Waste Identification Tag"** identifying the type of waste and the hazards associated with it. Hazardous Waste Identification Tags can be obtained from the Health & Safety Programs Unit (777-5269). Unidentified chemicals cannot be accepted for disposal by the Health & Safety Programs Unit (see subparagraph (e) below). 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.*). Waste pick-up by the Health & Safety Programs Unit is on a call-in basis; weekly pick-ups can be arranged if needed.

### (b) Liquid Organic Chemicals

The local regulations that govern the USC 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. Liquid organic chemicals should be stored in appropriate containers as outlined above and picked up for disposal by the USC Health & Safety Programs Unit. *Compatible* mixtures of liquid organic compounds can be stored in one container provided that the Hazardous Waste Identification Tag indicates the relative proportion of each component. *Halogenated compounds (e.g., chloroform) should be segregated in separate containers from other organic compounds.* Note that chlorinated solvents form explosive mixtures with certain other compounds (*e.g., with some amines, with acetone in the presence of base, etc.*). Ethereal solvents (diethyl ether, tetrahydrofuran (THF), dioxane, dimethylether (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 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 picked up by the staff of the Health & Safety Programs Unit in their original containers. Compatible solids can be stored in one container provided that the Hazardous Waste Identification Tag indicates the relative proportion of each component. Certain classes of solid waste chemicals require special handling. **Toxic solid wastes** should be left for pick-up in properly labeled, tightly sealed containers. Contact the USC Health & Safety Programs Unit for advice on the handling and packaging of toxic waste chemicals or for information on the properties and toxicity of organic and inorganic chemicals. **Alkali metals** such as sodium and potassium should be stored under mineral oil in tightly sealed containers and disposed of by the Health & Safety Programs Unit (777-5269). 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 picked up by the USC Health & Safety Programs Unit for disposal. Waste **mercury** should be stored in bottles or jars and picked up by the USC Health & Safety Programs Unit; broken thermometers that contain mercury should be placed in jars and also picked up by the USC Health & Safety Programs Unit.

# (e) Unidentified Waste Chemicals

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

# (f) Gas Cylinders

Excess and empty gas cylinders should be brought to the Chemistry Stockroom (777-2396) which has the responsibility of returning cylinders to the proper vendor. Most non-returnable, small "lecture-bottle-type" cylinders will also be accepted for disposal by the USC Health & Safety Programs Unit. For information on the disposal of these non-returnable cylinders, call USC Health & Safety Programs Unit at 777-5269. Whenever possible, avoid purchasing chemicals in non-returnable lecture bottles. The disposal of these cylinders has become extremely expensive, and will generally cost between \$300 and \$500!

The disposal of several other categories of excess and waste materials is governed by special regulations. Materials of this type include: controlled drugs, radioactive materials, biological wastes, and polychlorinated biphenyls. USC Health & Safety Programs Unit at 777-5269 will also supply information on handling and disposal of these materials.

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

It is USC 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, unknowledgeable, 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. The Health & Safety Programs Unit, Campus Police, or Columbia Fire Department will provide technical advice and will assist in spill clean up if necessary. Spills of large amounts of hazardous substances require immediate evacuation and notification of the USC Health & Safety Programs Unit and campus police for emergency response.

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

1. Tend to any injured or contaminated Personnel and if necessary request help (call the Campus Police at 777-9111).

2. Notify other personnel of the accident and if necessary evacuate the area. The Department of Chemistry & Biochemistry Office (777-5264), Dr. Michael D. Dukes, Assistant Chair (777-5264, 777-2687), or the Chemical Hygiene Officer (Dr. S. L. Morgan, GSRC 208, 777-2461) should be notified of any spill of hazardous substance.

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 materials properly according to the procedures described in sections 10 and 11 of Part VI.C above.

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

#### (a) Preplanning to Control Spills

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

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

(1) **Spill control pillows** (commercially available from Lab Safety Supply, American Scientific Products, and other companies). These generally can be used for absorbing solvents, acids, caustic alkalis, but not hydrofluoric acid (HF).

- (2) Inert absorbents such as vermiculite, clay, and sand.
- (3) Neutralizing agents for acid spills such as sodium carbonate and sodium bicarbonate.
- (4) Neutralizing agents for alkali spills such as sodium bisulfate.
- (5) Large plastic scoops and other equipment such as brooms, pails, bags, dustpans, etc. as appropriate.

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

If an individual is injured or contaminated with a hazardous substance, then tending to them will generally take priority over the spill control measures outlined below. It is important to obtain medical attention as soon as possible; call 777-9111, the Campus Police 24 hour line in the event of an emergency.

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

For splashes into the eye, immediately flush the eye with potable water for at least 15 minutes. While the eyelids are held open, the affected person should move the eye up and down and sideways to wash thoroughly. 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 medical evaluation of the eye(s), preferably by a physician acquainted with eye injuries and alerted to the nature of the hazardous substances. When medical services are warranted, on either an emergency or ultimate referral basis, notify Occupational Health Services at 777-3472 or 777-9057.

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

Alert other workers in the laboratory of the accident and the nature of the chemicals involved. In the event of the release of a highly toxic gas or volatile material, evacuate the laboratory (or building) by activating the nearest fire alarm and post personnel at entrances to prevent other workers from inadvertently entering the contaminated area Call 777-9111 to obtain

emergency assistance from the USC Campus Police and USC Health & Safety Programs Unit. Also call the Chemistry Office at 777-5264 to inform the Department administrators of the problem.

# (d) Clean up Spills Promptly

Specific procedures for cleaning up spills will vary depending on the location of the accident (elevator, corridor, chemical storeroom, laboratory hood), the amount and physical properties of the spilled material (volatile liquid, solid, or toxic gas), and the degree and type of toxicity. Outlined below are some general guidelines for handling several common spill situations.

(1) **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 bisulfate (for alkalis) and sodium carbonate or bicarbonate (for acids). Absorb the material with inert clay or vermiculite, scoop it up, and dispose of it according to the procedures detailed above in Part VI.C, section (11).

(2) **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 spill control pillows. These should be sealed in containers and disposed of properly.

(3) **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 USC Health & Safety Programs Unit (777-5269) to obtain assistance in evaluating the hazards involved. The USC Campus Police and Columbia Fire Department have special protective equipment to permit safe entry into areas contaminated with highly toxic substances.

# (e) Handling Leaking Gas Cylinders.

Occasionally, a cylinder or one of its component parts develops a leak. Most such leaks occur at the top of the cylinder in areas such as the valve threads, safety device, valve stem, and valve outlet. If a leak is suspected, do not use a flame for detection; rather, a flammable-gas leak detector or soapy water or other suitable solution should be used. If the leak cannot be remedied by tightening a valve gland or a packing nut, emergency action procedures should be effected and the Department of Chemistry & Biochemistry Chemical Stockroom (Ms. Vickie Ferguson, 777-2396) or 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. If feasible, leaking cylinders should be moved into laboratory hoods.

(1) **Flammable, inert, or oxidizing gases.** Move the cylinder to an isolated area (away from combustible material if the gas is flammable or an oxidizing agent) and post signs that describe the hazards and state warnings.

(2) **Corrosive gases** may increase the size of the leak as they are released and some corrosives are also oxidants or flammable. Move the cylinder to an isolated, well-ventilated area and use suitable means to direct the gas into an appropriate chemical neutralizer. Post signs that describe the hazards and state warnings.

(3) **Toxic gases** - Follow the same procedure as for corrosive gases. Move the cylinder to an isolated, well-ventilated area and use suitable means to direct the gas into an appropriate chemical neutralizer. Post signs that describe the hazards and state the warnings.

When the nature of the leaking gas or the size of the leak constitutes a more serious hazard, self-contained breathing apparatus and protective apparel may be required. Evacuate personnel from the affected area (activate the fire alarm to order the evacuation of the building) and call Campus Police (dial 777-9111) to obtain emergency assistance.

#### D. 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 Department of Chemistry & Biochemistry. 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.

Chemical	Flash Point (°C)	
Distingly other	45.0	
Dietnyl ether	-43.0	
Pentane	-40.0	
Carbon disulfide	-30.0	
Hexane	-21.7	
Cyclohexane	-20.0	
Acetone	-17.8	
Benzene	-11.1	
Toluene	4.4	
Methanol	11.1	
Ethanol	12.8	

#### (1) 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 electrically grounding the metal container with a grounding strap.

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.

#### (2) Handling Explosive Substances

Explosive substances are materials that decompose under conditions of mechanical shock, elevated temperature, or chemical action, with the release of large volumes of gases and heat. Special precautions are required for the safe use of explosive materials. *It is the responsibility of researchers to evaluate the explosive hazards involved in their work and to consult with their supervisors 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 Department of Chemistry & Biochemistry laboratories. As a class, they are low-power explosives, hazardous because of their sensitivity to shock, sparks, and even friction (as in a cap being twisted open). Many peroxides that are routinely handled in laboratories are far more sensitive to shock than most primary explosives such as TNT. All organic peroxides are highly flammable, and most are sensitive to heat, friction, impact, light, as well as strong oxidizing and reducing agents.

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

(a) Aldehydes including acetaldehyde and benzaldehyde,

(b) **Ethers** with primary and/or secondary alkyl groups, including acyclic and cyclic ethers, acetals, and ketals. Examples include diethyl ether, diisopropyl ether (especially dangerous!), dioxane, DME, THF, ethyl vinyl ether and alcohols protected as THP ethers. Isopropyl alcohol also frequently forms peroxides upon storage.

(c) **Hydrocarbons with allylic, benzylic, or propargylic hydrogens.** Examples of this class of peroxide-formers include cyclohexene, cyclooctene, methyl acetylene, isopropylbenzene (cumene), and tetralin (tetrahydronaphthalene).

(d) **Conjugated dienes, eneynes, and diynes,** among which divinylacetylene is particularly hazardous. Other materials such as 1,4-butadiene (usually supplied in a gas cylinder) form peroxides on contact with air. Various epoxides and other compounds such as ethylene oxide are also peroxide formers.

(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 Health & Safety Programs Unit (777-5269) for assistance in disposal.

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 potassium iodide (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 hydrochloric acid (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 D. R. Burfield, *J. Org. Chem.* **1982**, *47*, 3821. To destroy small quantities (25 g or less) of peroxides, dilute with water (to a concentration of 2% or less) and then transfer to an aqueous solution of an appropriate reducing agent (such as ferrous sulfate or sodium bisulfite) in a polyethylene container.

For assistance in disposing of larger quantities of peroxides or other explosive materials, contact the Health & Safety Programs Unit at 777-5269.

# (3) Control of Fires

USC 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.

**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.

Fires in small vessels can usually be suffocated by loosely covering the vessel. Never pick up a flask or container of burning material.

A **small fire that has just started** can sometimes be extinguished with a laboratory fire extinguisher. *Extinguishing such fires should only be attempted if you are confident that you can do so successfully and quickly, and from a position in which you are always between the fire and an exit from the laboratory.* Do not underestimate fires, and remember that toxic gases and smoke may present additional hazards. Do not attempt to extinguish a fire that has burned for more than 30 seconds.

**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 V.E), or by covering with dry sand.

In the event of a more serious fire, evacuate the laboratory and activate the nearest fire alarm. Be prepared to meet and advise personnel from the Columbia Fire Department and USC Health & Safety Programs Unit with regard to hazardous substances in your laboratory.

# (4) Personal injuries involving fires

If a person's clothing catches on fire, they should be doused with water from the safety shower. Minor clothing fires can sometimes be extinguished by immediately dropping to the floor and rolling. 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. See page 2 for the guidelines on emergency notification. If major chemical contamination of the body surface has occurred, continue submersion of the entire body in the safety shower for at least 15 minutes.

#### (5) 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 Department of Chemistry & Biochemistry laboratories. This list is not intended to be complete, and researchers should always be familiar with the flammability and other properties of the chemicals involved in their research.

1. Acetylenic compounds are explosive in mixtures of 2.5-80% with air. At pressures of 2 or more atmospheres, acetylene subjected to an electrical discharge or high temperature decomposes with explosive violence. Dry acetylides can detonate on receiving the slightest shock. Many heavy metal acetylides are sensitive explosives.

2. 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.

3. **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.

4. Dry **benzoyl peroxide** is easily ignited and sensitive to shock and may decompose spontaneously at temperatures above 50 °C. Benzoyl peroxide is reported to be desensitized by addition of 20% water.

5. 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 a glowing light bulb.

6. Chlorine may react violently with hydrogen or with hydrocarbons when exposed to sunlight.

7. **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 from this standpoint

8. **Dimethyl sulfoxide** decomposes violently on contact with a wide variety of active halogen compounds. Explosions from contact with active metal hydrides have been reported, probably because of water impurity, *i.e.*, wet DMSO.

9. **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.

10. **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.

11. **Halogenated compounds** such as chloroform, carbon tetrachloride, and other halogenated solvents should not be dried with sodium, potassium, or other active metals; violent explosions are usually the result of such attempts.

12. **Hydrogen peroxide** stronger than 3% can be dangerous; in contact with the skin, it may cause severe burns. Thirty percent hydrogen peroxide may decompose violently if contaminated with iron, copper, chromium, or other metals or their salts.

13. Liquid-nitrogen cooled traps open to the atmosphere rapidly condense liquid air. Then, when the coolant is removed, an explosive pressure buildup occurs, usually with enough force to shatter glass equipment. Hence, only sealed or evacuated equipment should be cooled.

14. **Lithium aluminum hydride** should not be used to dry methyl ethers or tetrahydrofuran; fires from this are very common. The products of its reaction 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.

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

15. **Ozone** is a highly reactive and toxic gas. It is formed by the action of ultraviolet light on oxygen (air) and, therefore, certain ultraviolet sources may require venting to the exhaust hood. Liquid and solid ozone are explosive substances.

16. **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. Particularly in 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. 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.

17. **Parr bombs** used for hydrogenations have been known to explode. They should be handled with care behind shields, and the operator should wear goggles. Hydrogenation bombs should not be filled from a gas cylinder using only a needle valve. If pressure limits (cited in the manufacturer's literature) for a controlled-atmosphere reaction chamber are exceeded, high-pressure rupturing of the container may result. A pressure regulator (preferably two-stage) should be used to avoid over-pressurizing the bomb.

18. **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 in proximity to a dehydrating acid strong enough to concentrate perchloric acid to more than 70% strength (*e.g.*, in a drying train that has a bubble counter containing sulfuric acid). Safer drying agents should be used. Seventy percent perchloric acid can be boiled safely at approximately 200 °C, but contact of the boiling undiluted acid or the hot vapor with organic matter, or even easily oxidized inorganic matter (such as compounds of trivalent antimony), will lead to explosions. Oxidizable substances must never be allowed to contact perchloric acid. Beaker tongs, rather than rubber gloves should be used when handling fuming perchloric acid. Perchloric acid evaporations should be carried out in a hood that has a good draft and a built-in water spray for ductwork behind the baffle. Frequent (weekly) washing of the hood and ventilator ducts with water is needed to avoid danger of spontaneous combustion or explosion if this acid is in common use. Metal perchlorates salts that are dried can also detonate upon shock.

19. **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.

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

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

22. **Phosphorus trichloride** reacts with water to form phosphorous acid that 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.

23. **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 the metal. Explosions can occur otherwise.

24. **Residues from vacuum distillations** have been known to explode when the still was vented to the air before the residue was cool. Such explosions can be avoided by venting the still pot with nitrogen, by cooling it before venting, or by restoring the pressure slowly.

25. **Selenium** reacts with incandescence with metals (nickel, sodium, potassium, phosphorus, uranium, zinc, and platinum); the particle size of cadmium and selenium must be below a critical size to prevent explosions when making cadmium selenide—this also applies to zinc and selenium; oxidation of recovered selenium with nitric acid is made vigorous by the presence of organic impurities; selenium may react explosively with BrF<sub>5</sub>, ClF<sub>3</sub>, N<sub>2</sub>O<sub>2</sub>, or Na<sub>2</sub>O<sub>2</sub>; it also ignites on contact with fluorine (F<sub>2</sub>). Selenium initiates a violent and often explosive decomposition of nitrogen trichloride (NCl<sub>3</sub>). Heating selenium in oxygen in the presence of organic impurities may result in a vigorous explosion.

26. **Sodium** should be stored in a closed container under kerosene, toluene, or mineral oil. Scraps of sodium (Na) or potassium (K) should be destroyed by reaction with n-butyl alcohol. Contact with water should be avoided because Na reacts violently with water to form hydrogen with evolution of sufficient heat to cause ignition. Carbon dioxide, bicarbonate, and carbon tetrachloride fire extinguishers should not be used on alkali metal fires.

### (6) Incompatible Chemicals

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 with which it is incompatible. Such contact could result in an explosion or the formation of substances that are highly toxic or flammable or both. The following Table is a guide to avoiding accidents involving **incompatible substances**.

Chemical	Is Incompatible With
Acetic acid	Chromic acid, nitric acid, perchloric acid, peroxides, permanganates
Acetylene	Chlorine, bromine, copper, fluorine, silver, mercury
Acetone	Concentrated nitric acid and sulfuric acid mixtures.
Alkali and alkaline earth metals (such as powdered aluminum or magnesium, calcium, lithium, sodium, potassium)	Water, carbon tetrachloride or other chlorinated hydrocarbons, carbon dioxide, halogens
Ammonia (anhydrous)	Mercury (in manometers, for example), chlorine, calcium hypochlorite, iodine, bromine, hydrofluoric acid (anhydrous)

#### Examples of Incompatible Chemicals

Chemical	Is Incompatible With	
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	
Chlorates	Ammonium salts, acids, powdered metals, sulfur, finely divided organic or combustible materials	
Chromic acid and chromium trioxide	Acetic acid, naphthalene, camphor, glycerol, alcohol, flammable liquids in general	
Chlorine	Ammonia, acetylene, butadiene, butane, methane, propane (or other petroleum gases), hydrogen, sodium carbide, benzene, finely divided metals, turpentine	
Chlorine dioxide	Ammonia, methane, phosphine, hydrogen sulfide	
Copper	Acetylene, hydrogen peroxide	
Cumene hydroperoxide	Acids (organic or inorganic)	
Decaborane	Carbon tetrachloride and some other halogenated hydrocarbons	
Flammable liquids	Ammonium nitrate, chromic acid, hydrogen peroxide, nitric acid, sodium peroxide, halogens	
Fluorine	Everything	
Hydrofluoric acid (anhydrous)	Ammonia (aqueous or anhydrous)	
Hydrogen peroxide	Copper, chromium, iron, most metals or their salts, alcohols, acetone, organic materials, aniline, nitromethane, combustible materials	
Hydrogen sulfide	Fuming nitric acid, oxidizing gases	
Hypochlorites	Acids, activated carbon	
Iodine	Acetylene, ammonia (aqueous or anhydrous), hydrogen	

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

# Part VII. Procedures for Work with Particularly Hazardous Substances

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

As discussed in the previous section (Part VI) of this Chemical Hygiene Plan, hazardous chemicals are chemicals for which there is scientific evidence that adverse acute or chronic health effects may occur in exposed workers.

An agent is an **acute toxin** if its toxic effects are manifested after a single or short-duration exposure.

**Chronically toxic agents** show their effects after repeated or long duration exposure and the effects usually become evident only after a long latency period. Many of the substances in frequent use in the Chemistry Department are classified as *hazardous substances*, and the procedures for working with these chemicals are detailed in Part VI.

There are some substances, however, that pose such significant threats to human health that they are classified as "particularly hazardous substances" (PHSs). The OSHA Laboratory Standard requires that special provisions be established to prevent the harmful exposure of researchers to PHSs. General procedures for working with such materials are presented in detail in Parts VII.C and VII.D below. Three categories of *Particularly Hazardous Substances* are defined in the OSHA Lab Standard.

#### 1. Select Carcinogens

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

(a) It is regulated by OSHA as a carcinogen,

(b) It is listed as "known to be a carcinogen" in the latest *Annual Report on Carcinogens* published by the National Toxicology Program (NTP),

(c) It is listed under Group 1 ("carcinogenic to humans") by the *International Agency for Research on Cancer* (IARC), or

(d) It is listed under IARC Group 2A or 2B, ("probably carcinogenic to humans") or under the category "reasonably anticipated to be a carcinogen" by the NTP, *and* causes statistically significant tumor incidence in experimental animals after:

- (i) inhalation exposure of 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) repeated skin application of less than 300 mg/kg of body weight per week; or
- (iii) oral dosages of less than 50 mg/kg of body weight per day.

The table below lists the substances meeting criteria (a), (b), or (c). For information on compounds meeting criteria (d), see copies of the IARC Group 2A and 2B lists and the NTP lists (available in the Safety Library located in the Departmental Mass Spectrometry Laboratory).

Partial List of Select Carcinogens (chemicals in common use in **bold**)

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

#### 2. Reproductive Toxins

Reproductive toxins act during pregnancy and cause adverse effects on the fetus; these effects include embryolethality (death of the fertilized egg, embryo or fetus), malformations (teratogenic effects), and postnatal functional defects. Examples of embryotoxins include thalidomide, and physical agents such as radiation. Women of childbearing potential should note that embryotoxins have the greatest impact during the first trimester of pregnancy. Because a woman often does not know that she is pregnant during this period of high susceptibility, special caution is advised when working with all chemicals, especially those rapidly absorbed through the skin (*e.g.*, **formamide**, **DMSO**, *etc.*). Pregnant women and women intending to become pregnant should consult with their laboratory supervisor and Occupational Health Services before working with substances that are suspected to be reproductive toxins. As minimal precautions, the general procedures outlined in Part VII.C below should be followed for work with such compounds.

The following table lists some common materials that are highly suspected to be reproductive toxins.

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

Partial List of Reproductive Toxins (chemicals in common use in bold)

The above list is not intended to be complete, and it is the responsibility of researchers (in consultation with their laboratory supervisors) to evaluate each compound involved in their work and to determine whether it should be handled as a reproductive toxin. Women who are pregnant or are planning for pregnancy should review this section regularly.

# 3. Compounds with a High Degree of Acute Toxicity

Compounds that have a high degree of acute toxicity comprise a third category of particularly hazardous substances as defined by the OSHA Lab Standard. Acutely toxic agents include certain corrosive compounds, irritants, sensitizers (allergens), hepatotoxins, nephrotoxins, neurotoxins, agents that act on the hematopoietic systems, and agents which damage the lungs, skin, eyes, or mucous membranes (see Part VI.B 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 (see Table below and Part XIII), and substances which "may be fatal or cause damage to target organs as the result of a single exposure or exposures of short duration."

$LD_{50}$ for albino rats	Toxic	Highly toxic
Oral	50-500 mg/kg	<50 mg/kg
Skin Contact	200-1000 mg/kg	< 200 mg/kg
Inhalation	200-2000 ppm/air	<200 ppm/air

Some of the compounds in current use research laboratories and which have a high degree of acute toxicity are listed below.

Partial List of Compounds with a High Degree of Acute Toxicity (chemicals in common use in **bold**)

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

The above list is not intended to be complete, and it is the responsibility of the researcher (in consultation with their laboratory supervisor) to evaluate each compound involved in their work and to determine whether it is a substance with a high degree of acute toxicity. Compounds so classified generally must then be handled using the procedures outlined in Part VII.C. Note, however, that in some circumstances (*e.g.*, when very small quantities of material are being used) it may not be necessary to employ all of the special precautions described in Part VII.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 VIII 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 a toxic compound. For example, people are rarely exposed to a single biologically active substance. With this point in mind, it is noteworthy that one toxin can influence the effect of a second. Several classic examples are the dramatically enhanced lung carcinogenicity of combined exposure to asbestos and tobacco smoke, and the potentiating activity of phorbol esters on skin carcinogenesis initiated by polycyclic hydrocarbons. There are insufficient data at present to identify which substances potentiate (or possibly even antagonize) the effects of others, but is important for laboratory workers to be cognizant that such interactions can occur. This point underscores the importance of maintaining good laboratory practices at all times, and with all chemicals.

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

#### **B.** Designated Areas

A key requirement of the OSHA Laboratory 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 substances in use there.

It is the responsibility of laboratory supervisors to define the designated areas in their laboratories. These areas shall be posted with conspicuous signs reading "DESIGNATED AREA FOR USE OF PARTICULARLY HAZARDOUS SUBSTANCES—AUTHORIZED PERSONNEL ONLY". Printed signs can be obtained from Dr. Stephen L. Morgan (Chemical Hygiene Officer, GSRC 208, 777-2461). In some cases it may be appropriate to post additional signs describing unusual hazards present and/or identifying the specific hazardous substances in use.

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

# C. General Procedures for Work with Substances or 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 VII.D below. Keep in mind that the general rules for work with toxic substances discussed in Part VI.C of this Chemical Hygiene Plan also apply to work with "Particularly Hazardous Substances".

# (1) Information

Before beginning a laboratory operation, each researcher should consult the appropriate literature (see Part IV and references in Part XII) 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 VII.D.

# (2) Zero skin contact

Contact with the skin is a frequent mode of 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) or gauntlets (long gloves) and a suitable laboratory coat or apron which covers all exposed skin. See Part V.B for a further discussion of protective apparel. Always wash your hands and arms with soap and water immediately after working with these materials. In the event of accidental skin contact, the affected areas should be flushed with water and medical attention should be obtained as soon as possible.

# (3) Use laboratory hoods

Inhalation of toxic vapors, mists, gases, or dusts can produce poisoning by absorption through the mucous membrane of the mouth, throat, and lungs, and can seriously damage these tissues by local action. Inhaled gases or vapors may pass rapidly into the capillaries of the lungs and be carried into the circulatory system. This absorption can be extremely rapid. *Procedures involving volatile toxic substances and those operations involving solid or liquid toxic substances that may result in the generation of aerosols must be conducted in a hood or other suitable containment device.* The hood should have been evaluated previously to establish that it is providing adequate ventilation and has an average face velocity of not less than 80 linear ft/min. See Part V.D 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 sorbent plastic-backed paper. Such procedures will contain spilled toxic substances in a pan, tray, or sorbent liner and greatly simplify subsequent cleanup and disposal.

If a major release of a particularly hazardous substance occurs outside the hood, then the room or appropriate area should be evacuated and necessary measures taken to prevent exposure of other workers. Call USC Health & Safety Programs Unit (777-5269) for assistance and equipment for spill clean-up; personnel can be contacted for assistance after working hours by

calling Campus Police (777-9111). 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 VI.C.12 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 VI.C.11 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, impermeable 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 half-filled with vermiculite. All containers of toxic wastes should be suitably labeled to indicate the contents (chemicals and approximate amounts) and the type of toxicity hazard that contact may pose. For example, containers of wastes from experiments involving appreciable amounts of weak or moderate carcinogens should carry the warning: CANCER SUSPECT AGENT. All wastes and residues that have not been chemically decontaminated in the exhaust hood where the experiment was carried out should be disposed of in a safe manner that ensures that personnel are not exposed to the material.

#### (6) Record keeping

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

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

Those operations involving particularly hazardous substances in which there is the possibility of accidental release of harmful quantities of the toxic substance must be carried out in designated areas As discussed in Part VII.B, in the Department of Chemistry & Biochemistry 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 such as dimethylmercury and nickel carbonyl. See Section VII-A for a more detailed discussion of the identification of substances with high chronic toxicity.

# (1) Approvals

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

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

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

All experiments with and transfers of such substances or mixtures containing such substances should be done in a designated area such as an 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. If gases are vented from a glove box, they should be passed through a suitable trap or filter or directly into the hood system. Laboratory vacuum pumps used with substances having high chronic toxicity should be protected by high-efficiency scrubbers or HEPA filters and vented into an exhaust hood. Motor-driven vacuum pumps are recommended because they are easy to decontaminate. (*Note:* decontamination of a vacuum pump should be carried out in an exhaust hood). Designated areas should be clearly marked with a conspicuous sign reading: DESIGNATED AREA FOR USE OF PARTICULARLY HAZARDOUS SUBSTANCES—AUTHORIZED PERSONNEL ONLY. Only authorized and instructed personnel should be allowed to work in or have access to such designated areas.

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

or absorbent paper liners have been used, these items should generally 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. Nondisposable 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 either decontaminated chemically or placed in closed, suitably labeled containers for incineration. If chemical decontamination is to be used, a method should be chosen that can reasonably be expected to convert essentially all of the toxic materials into nontoxic materials. For example, residues and wastes from experiments in which  $\beta$ -propiolactone, *bis*(chloromethyl)ether, or methyl chloromethyl ether have been used should be treated for 10 min with concentrated aqueous ammonia. In the event that chemical decontamination is not feasible, wastes and residues should be placed in an impermeable container that should be closed and labeled in some manner such as the following: CAUTION: COMPOUNDS OF HIGH CHRONIC TOXICITY or CAUTION: CANCER SUSPECT AGENT. In general, liquid wastes containing such compounds should be placed in glass or (usually preferable) polyethylene bottles half filled with vermiculite 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 Health & Safety Programs Unit (777-5269) 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 that may occur. The Health & Safety Programs Unit (777-5269) 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 at the Occupational Health Services (777-3472) should be consulted to determine whether it is advisable to establish a regular schedule of medical surveillance or biological monitoring. See Part IX for a further discussion of medical surveillance.

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

This section outlines special handling procedures for some specific particularly hazardous substances that may be used in Department of Chemistry and Biochemistry 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 (CH<sub>2</sub>CHCN)

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-min period. Dermal or eye contact with liquid acrylonitrile is also prohibited. *Work involving significant quantities of acrylonitrile should be conducted using the general procedures outlined in both Parts VI-C and VI-D*. Laboratory hoods that have been demonstrated to provide sufficient protection should be used, and closed systems are recommended for laboratory operations.

# (2) Benzene (C<sub>6</sub>H<sub>6</sub>)

In humans, acute inhalation exposure to benzene can produce a picture of acute delirium, characterized by excitement, euphoria, and restlessness and, if the exposure is significantly high, the symptoms may progress to depression, drowsiness, stupor, and even unconsciousness. The concentration required to produce this symptom complex is 1000 ppm or higher. These concentrations will also produce irritation of the eye, nose, and respiratory tract. Chronic inhalation exposure to 25-50 ppm of benzene can produce changes in the blood picture that include macrocytosis, decrease in the total red blood count, decrease in platelets, decrease in the hemoglobin concentration, or decrease in leukocytes. Any or all of these hematologic effects may be seen in any individual. Usually, the worker will be asymptomatic while these effects are observed in the blood picture. Continued exposure at somewhat higher concentrations (probably more than 100 ppm) can insidiously result in a more severe blood disorders that include leukopenia or even aplastic anemia, with symptoms of headaches, dizziness, loss of appetite, nervousness, irritability, and perhaps bleeding manifestations, *i.e.*, nosebleeds, easy bruisability, or hematuria. Severe cases may have fatal outcomes. Benzene is designated as a "Human Carcinogen" (OSHA).

Recently, a number of reports have been published that describe leukemia in workers who have had aplastic anemia. These cases have been reported in Italy and Turkey in workers exposed to grossly high concentrations of benzene. In addition, there is some indication that an excess of leukemia may occur without a preceding picture of aplastic anemia in workers who have been repeatedly exposed to benzene at concentrations of more than 100 ppm.

The current OSHA PEL for benzene is 10 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 benzene should be conducted employing the general procedures outlined in Part VII.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:  $LD_{50}$  (rats, 7-hour inhalation) = 7 ppm. It is moderately toxic via the oral and skin routes:  $LD_{50}$  (rats, oral) = 280 mg/kg;  $LD_{50}$  (rabbits, skin) = 368 mg/kg. Its vapors are strongly irritating to the eyes of rats. Rats and hamsters subjected to 10 or 30, 6-hour exposures of 1 ppm BCME showed evidence of tracheal and bronchial hyperplasia, as well as effects on the central

nervous system. BCME is carcinogenic to mice following inhalation, skin application. or subcutaneous administration. In newborn mice, it is carcinogenic by inhalation and subcutaneous administration. BCME is a lung carcinogen in humans.

The TLV for BCME is 0.001 ppm (1 ppb; 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 with the general procedures outlined in Parts VI-C and VI-D*.

#### (4) Carbon Monoxide (CO)

Carbon monoxide is a direct and cumulative poison. It combines with the hemoglobin of the blood to form a relatively stable compound, carboxyhemoglobin, and renders 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 that have adequate ventilation employing the general procedures outlined in Part VII.C.* A trap or vacuum break should always be used to prevent impurities from being sucked back into a CO cylinder.

#### (5) Carbon Tetrachloride (CCl<sub>4</sub>)

The current OSHA PEL and TLV for carbon tetrachloride are 10 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 min 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 min 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 toxic responses.

The carcinogenic potency of carbon tetrachloride is low and in *most of its uses in Department of Chemistry & Biochemistry 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 VII.C should provide adequate protection. All operations should be carried out in a hood, not only because of the carcinogenicity of the substance, but also because of its other toxic effects and its volatility. Nitrile rubber is the recommended material for gloves and other protective clothing. As a closing note: the toxicity of CCl<sub>4</sub> is enhanced synergistically if alcohol is consumed after exposure.

#### (6) Chlorine (Cl<sub>2</sub>)

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. Minimal irritation of the throat and nose are noticed at about 2.6 ppm and painful irritation at about 3.0 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 1 ppm (3 mg/m<sup>3</sup>) as a ceiling. NIOSH has recommended a ceiling limit of 0.5 ppm over any 15-min period. The ACGIH 15-min exposure limit is 3 ppm.

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

# (7) Chloroform (CHCl<sub>3</sub>)

Inhalation exposure to chloroform at concentrations greater than 1000 ppm can produce dizziness, nausea, and headaches. At higher concentrations, there can be disorientation and delirium progressing to unconsciousness. Such high exposure can also produce liver and possibly kidney damage. It is believed that chloroform can sensitize the heart to adrenaline, so it may cause cardiac arrhythmias and possibly death. High concentrations of the vapor can produce conjunctivitis. Liquid chloroform in the eyes will produce a painful corneal injury that usually heals in several days. Chronic exposure to chloroform at concentrations of 100-200 ppm has been reported to produce large livers. Continued contact with the skin can produce drying, fissuring, and inflammation. In experimental studies, prolonged ingestion of high levels of chloroform by mice resulted in liver cancers and by rats, kidney tumors.

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 plus a base, aluminum, disilane, lithium, magnesium, nitrogen tetroxide, potassium, perchloric acid plus phosphorus pentoxide, potassium hydroxide plus methanol, potassium *t*-butoxide, sodium, sodium hydroxide plus methanol, sodium methylate, or 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-min period. The ACGIH currently recommends that chloroform be treated as a suspect human carcinogen and recommends an 8-hour time weighted average exposure of 10 ppm.

Although chloroform has caused tumors in animals, its potency is low. *In most of its uses in the Department of Chemistry & Biochemistry 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 VII.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 Sulfate ((CH<sub>3</sub>)<sub>2</sub>SO<sub>4</sub>, DMS) and Diethyl Sulfate ((CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>SO<sub>4</sub>, DS)

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 possible painful eyes, nose and throat irritation, loss of voice, coughing, difficulty in breathing and swallowing, vomiting, and diarrhea. The onset of the symptoms may be delayed up to 10 hours. Skin contact causes blistering and necrosis, and DMS can be absorbed through the skin in sufficient quantity to cause systemic intoxication. In the worst cases, there is severe inflammation of the mucous membranes and pulmonary injury that may be fatal; several deaths have occurred. For example, exposure to 97 ppm for 10 min was fatal. DMS is moderately toxic to animals via the oral route:  $LD_{50}$  (rats) = 440 mg/kg. Undiluted DMS produced moderate to severe irritation when applied to the skin of guinea pigs; 1% DMS produced mild irritation. DMS does not cause skin sensitization in animals. Undiluted DMS applied to rabbit eyes produced severe injury. Even a 1-hour exposure to 58 ppm has resulted in permanent eye damage in rats. During a 4-hour exposure, 30 ppm DMS killed five out of six rats, but 15 ppm was not lethal.

DMS has been shown to be carcinogenic in the rat by inhalation, subcutaneous injection, and following 1 hour per day exposures to 10 ppm DMS for 130 days. The TLV 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 absorption to the overall exposure.

The general procedures outlined in Part VII.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 appropriate use of rubber gloves, a rubber apron, and other protective apparel, and to avoid inhalation of even low concentrations of vapor by working in a hood. Operations involving smaller quantities of DMS can be conducted using the general procedures presented in Part VII.C.

# (9) Ethylene Dibromide (l,2-Dibromoethane, EDB)

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 absorption of EDB can also cause death, and inhalation of the vapor can produce pulmonary edema. EDB can cause severe irritation to all exposed tissues, respiratory tract, skin, and eye. Systemic effects

include central nervous system depression, kidney injury, and severe liver necrosis. Ethylene dibromide is highly toxic to animals via inhalation. The maximum survival exposure of rats to EDB vapors in air is 3000 ppm for 6 min, 400 ppm for 30 min, and 200 ppm for 2 hours. It is moderately toxic via the oral and skin routes: 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 in rabbit eyes. Rats were repeatedly exposed to 50 ppm EDB for 6 months. Half died from pneumonia and upper respiratory tract infections. Slight changes in the liver and kidney were seen. EDB has induced a high incidence of tumors (squamous-cell carcinomas of the forestomach) in mice and rats following oral administration. The 1979 TLV 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-min period. These limits include a warning about the potential contribution of skin absorption to the overall exposure. In 1980, the ACGIH put EDB in category A 1b (human carcinogen). For this category, there is no assigned TLV, 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 min in any 8-hour time period.

On the basis of the carcinogenicity data for EDB, *the procedures described in Part VII.D should be followed when handling more than a few grams in the laboratory*. Operations involving smaller quantities should be carried out using the procedures outlined in Part VII.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 of these materials provide only temporary protection if EDB spills on them.

### (10) Hydrazine (H<sub>2</sub>NNH<sub>2</sub>)

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:  $LC_{50}$  (rats, 4-hour inhalation) = 570 ppm;  $LD_{50}$ (rats, oral) = 60 mg/kg;  $LD_{50}$ (rabbits, skin) = 283 mg/kg (hydrazine hydrate). It is a strong skin and mucous membrane irritant and a strong skin sensitizer. Hydrazine hydrate produced moderately severe irritation when applied to rabbit eyes. After repeated oral, skin, or injection exposure, the effects noted include weight loss, weakness, vomiting, and convulsions. The chief histological finding is fatty degeneration of the liver. Among guinea pigs and dogs exposed to hydrazine in the air 547 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 averages. These limits include a warning about the potential contribution of skin absorption to the overall exposure. NIOSH has (1978) recommended a ceiling limit of 0.03 ppm in any 2-hour period.

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

#### (11) Hydrogen Bromide (HBr) and Hydrogen Chloride (HCl)

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

Hydrogen bromide and hydrogen chloride are corrosive gases that have pungent, irritating odors. 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 act 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 with the general procedures outlined in Part VII.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 value packing nut (by turning it clockwise as viewed from above).

# (12) Hydrogen Cyanide (HCN)

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

# (13) Hydrofluoric Acid (HF)

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 [N. H. Proctor, J. P. Hughes, and M. L Fischman, 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 slowhealing skin ulcers.

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

Note that any  $BF_4^-$  salt in prolonged contact with glass containers will produce enough HF to etch glass and perhaps release HF gas.

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

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

**In the event of exposure**—Anyone who knows or even suspects that he or she has come into direct contact with HF should immediately flush the exposed area with large quantities of cool water. Exposed clothing should be removed as quickly as possible while flushing. Medical attention should be obtained promptly, even if the injury appears slight. On the way to the physician, the burned area should be immersed in a mixture of ice and water. If immersion is impractical, a compress made by inserting ice cubes between layers of gauze should be used. Make sure that the physician understands that the injury was caused by HF and requires treatment very different from other acid burns. Even in the case of very small exposure, washing alone may not be sufficient to completely prevent injury. For minor exposures such as small hole in a glove, application of a calcium glutaconate antidote gel can bind free fluoride ion not removed by washing. For regular HF users, this gel may be obtained by contacting Occupational Health Services (777-3472).

If HF liquid or vapor has contacted the eyes, the eyes should be flushed with large quantities of clean water while the eyelids are held apart. This flushing should be continued for at least 15 minutes. Medical attention should be obtained promptly.

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

Additional information on hydrofluoric acid exposure is available on the Departmental safety web site at: <u>http://www.chem.sc.edu/faculty/morgan/safety/hf.html</u>.

# (14) Hydrogen Sulfide (H<sub>2</sub>S)

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 min has caused unconsciousness, arm cramps, and low blood pressure. Coma may occur within seconds after one or two breaths at high concentrations and be followed rapidly by death. For example, workers exposed to 930 ppm H<sub>2</sub>S for less than 1 min died. Hydrogen sulfide is moderately toxic to animals via the inhalation route:  $LC_{50}$  (mice, 1 hour) = 673 ppm;  $LC_{50}$  (mice, 7.5 hours) = 140 ppm. Exposure to 10-13 ppm for 4-7 hours has caused eye irritation. Skin absorption of H<sub>2</sub>S 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% H<sub>2</sub>S vapors for 1 hour experienced slight swelling. The TLV for H<sub>2</sub>S is 10 ppm (14 mg/m<sup>3</sup>) as an 8-hour time-weighted average. The short-term exposure limit (15 min) is 15 ppm. The OSHA PEL has a ceiling limit of 20 ppm and a peak of 50 ppm over any 10-min period. NIOSH (1977) has recommended a 10-min ceiling of 10 ppm. Part of the danger of low exposure to H<sub>2</sub>S is that the sense of smell is impaired and dangerous levels may be reached without detection.

Partly because of the disagreeable odor of  $H_2S$ , but also because of its toxicity, laboratory operations with it should be carried out in a hood. Use the general procedures outlined in Part VII.C when working with hydrogen sulfide. Cylinders of  $H_2S$  should not be stored in small, unventilated rooms, as deaths have resulted from people entering such rooms containing a leaking cylinder.

# (15) Mercury (Hg)

The element mercury is a liquid metal with a vapor pressure of 0.00185 mm at 25 °C. This corresponds to a saturation concentration of 20 milligrams of mercury per cubic meter of air or 2.4 parts per million of air. The American Conference of Governmental Industrial Hygienists has established a threshold limit for mercury vapor of 0.05 milligrams of mercury per cubic meter of air for continuous 40-hour per week exposure. Long term chronic exposure to mercury vapor in excess of 0.05 mg of mercury per cubic meter of air may result in cumulative poisoning. The use of mercury in laboratory amounts in well-dilution-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 mercurial salts. In most cases of exposure by chronic inhalation, the symptoms of poisoning gradually disappear when the source of exposure is removed. However, improvement may be slow and complete recovery may take years. Skin contact with mercury compounds produces irritation and various degrees of corrosion. Soluble mercury salts can be absorbed through the intact skin and produce poisoning.

*The general procedures outlined in Part VII.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 Hg. 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 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 Health & Safety Programs Unit (777-5269) will be glad to survey the area and advise on the degree of hazard which may exist and necessary preventive 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 Hg from laboratory activities should be collected in thick-walled high-density polyethylene bottles for reclamation. Rags, sponges, shoe covers, and such used in clean-up activities, and broken thermometers containing small amounts of residual mercury, should be placed in a sealed plastic bag, labeled, and disposed of by the Health & Safety Programs Unit.

# (16) Metal carbonyl compounds (including nickel carbonyl (Ni(CO)4), iron carbonyl (Fe(CO)5), and osmium carbonyl (Os(CO)12)

*The use of carbonyl compounds requires prior approval from the Department of Chemistry & Biochemistry Chemical Hygiene Committee* (see Part VIII). Volatile carbonyl compounds are very dangerous. These compounds should not be handled in the laboratory outside a protective hood.

Most metal carbonyl cluster compounds (*e.g.*,  $Os_3(CO)_{12}$ ) are not especially volatile and crystalline forms may be examined under the microscope (*e.g.*, in room 319). Otherwise all metal carbonyl cluster compounds should be manipulated in the hoods or stored in sealed containers on bench tops or in the refrigerators when not in use.

# (17) Nitrogen Dioxide (NO<sub>2</sub>)

Nitrogen dioxide  $(N0_2)$  is classified as a highly acute toxin; it is a primary irritant, acting primarily 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 N0<sub>2</sub> 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. Toxic quantities of N0<sub>2</sub> can be produced whenever HN0<sub>3</sub> is used as an oxidizing agent.

*Nitrogen dioxide should be handled using the general procedures outlined in Part VII.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.

### (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 as a consequence of ingestion, inhalation, and topical application to the skin.

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

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

Clean-up of spills and waste disposal—Because N-nitrosodialkylamines are chemically stable under usual conditions, disposal is best carried out by incineration. Contact the Health & Safety Programs Unit (777-5269) to arrange for the disposal of waste and contaminated materials. For incineration of liquid wastes, solutions should be neutralized if necessary, filtered to remove solids, and put in closed polyethylene containers for transport. All equipment should be thoroughly rinsed with solvent, which should then be added to the liquid waste for incineration. Great care should be exercised to prevent contamination of the outside of the solvent container. If possible, solid wastes should be incinerated; if this is not possible, solid wastes from reaction mixtures that may contain N-nitrosodialkylamines should be extracted and the extracts added to the liquid waste. Similarly, any rags, paper and such that may be contaminated should be incinerated. Contaminated solid materials should be enclosed in sealed plastic bags that are labeled CANCER-SUSPECT AGENT and with the name and amount of the carcinogen. The bags should be stored in a well-ventilated area until they are incinerated. Spills of Nnitrosodialkylamines can be absorbed by Celite R or 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 Health & Safety Programs Unit (777-5269) 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 (COCl<sub>2</sub>)

Phosgene is classified as a substance with a high degree of acute toxicity. In humans, the symptoms of overexposure to phosgene are dryness or a burning sensation in the throat, numbness, vomiting, and bronchitis. An airborne concentration of 5 ppm may cause eye irritation and coughing in a few minutes. The substance can cause severe lung injury in 1-2 min at a level of 20 ppm. Exposure to concentrations above 50 ppm is likely to be fatal. Phosgene is extremely toxic to animals via inhalation. Thus, 74% of a group of rats died from exposure to 55-100 ppm for only 10 min. Liquid phosgene is likely to cause severe skin burns and eye irritation. Pulmonary edema, bronchiolitis, and emphysema were found in cats and guinea pigs exposed to 2.5-6.25 ppm of phosgene/day for 2-41 days. A variety of animals exposed to 0.2 or 1.1 ppm for 5 hours per day for 5 days also had pulmonary edema. The TLV and the OSHA PEL for phosgene are 0.1 ppm (0.4 mg/m<sup>3</sup>) as an 8-hour time-weighted average. NIOSH has recommended a limit of 0.2 ppm over any 15-min period. Note that phosgene gas is formed by the thermal decomposition of most chlorinated hydrocarbon compounds.

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

# (20) Selenium (Se) and its compounds

Selenium poses a serious risk of poisoning by inhalation or swallowing and there is serious danger of cumulative effects to exposure. Selenium is a steel gray or purplish powder, also fabricated into pellets, sticks or plates, insoluble in water. Selenium dioxide, selenous acid, and the alkali-metal selenites and selenates are colorless powders or crystals. Hydrogen selenide irritates the nose, eyes, and lung tissue, and disturbs the digestive and nervous systems. Solutions of selenium compounds may burn the skin and causes severe pain by skin absorption. Selenium dioxide dust irritates the respiratory system, eyes, and skin, and is particularly harmful by skin absorption. Swallowing will cause severe irritation and poisoning. Prolonged exposure to selenium dust may cause chronic effects such as dermatitis, fatigue, digestive upset, and bronchitis. Avoid breathing dust. Avoid contact with skin and eyes. TLV (selenium compounds as Se) 0.2 mg/m<sup>3</sup>.

**Cleanup of spills**—Selenium powder may be mixed with sand and treated as normal refuse, as may the disulfide. Soluble selenites and selenates can be dissolved in water and run to waste, diluting greatly with running water. Sodium carbonate should be applied liberally to spillages of selenium dioxide, selenic and selenous acids and selenyl and selenium chlorides, which may then be mopped up cautiously with plenty of water, this being run to waste, diluting greatly with running water.

**Waste disposal**—Packaged lots: place in separate labeled container for disposal. Small quantities: Wear rubber gloves, safety goggles, respirator, or work in hood, laboratory coat. Aqueous solutions of soluble salts should be made strongly acidic with hydrochloric acid. Slowly add sodium sulfite to the cold solution with stirring, thus producing sulfur dioxide, the reducer. Heat to form element. Allow to stand overnight. Filter, wash, dry, and recycle or send for disposal. Selenium or insoluble salts can be recycled or sent for disposal.

# (21) Sodium Cyanide (NaCN) 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:  $LD_{50}(rats) = 6.4 \text{ mg/kg}$ . It can be corrosive to the skin and the eyes, for it is highly alkaline. Sodium cyanide can also produce toxic symptoms via skin absorption and inhalation. The TLV 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 of 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 min ceiling.

Proper gloves should be worn when handling dry sodium cyanide. Rubber gloves and splash proof goggles should be worn when substantial amounts of sodium cyanide solution are used. Hydrolysis of sodium cyanide (and other cyanide salts) by water or acid generates HCN which is extremely hazardous. Consequently, *cyanide salts should always be handled using the* 

general procedures outlined in Part VII.C. All reaction equipment in which cyanides are used or produced should be placed in or over shallow pans so that spills or leaks will be contained. In the event of spills of HCN or cyanide solutions, the contaminated area should be evacuated promptly and it should be determined immediately whether anyone had been exposed to cyanide vapors or liquid splash. Consideration should be given to the need for evacuating other parts of the building or notifying other occupants that the spill has occurred. In general, it is usually best not to attempt to dilute or absorb such spills if they occur in well-ventilated areas.

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

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

**Waste disposal**—Waste solutions containing cyanides should be sealed in clearly marked bottles. Contact the Health & Safety Programs Unit 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 VIII. Prior Approval Requirements

The use of certain particularly hazardous substances requires the prior approval of the Department of Chemistry & Biochemistry Safety Committee. At the time of this writing, prior approval is required for work with the compounds listed below. Laboratories will be informed regarding any additions to this list.

# **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 Departmental Safety Committee. This plan should specify:

- 1. Procedures for routine handling and storage of the restricted chemical;
- 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 Professor Morgan (Chemistry Department Chemical Hygiene Officer, GSRC 208, phone 777-2461).

#### **Prior Approval from Laboratory Supervisor**

In the use of restricted chemicals, approval to proceed with a laboratory task should be obtained from the laboratory supervisor when:

1. there is a new procedure, process, or test, even if it is very similar to older practices;

2. there is a change or substitution of any of the ingredient chemicals in a procedures;

3. there is a substantial change in the amount of chemicals used; usually one should review safety practices if the volume of chemicals used increases by 20 or 25%;

4. there is a failure of any of the equipment used in the process, especially safeguards such as fume hoods or clamp apparatus;

5. there are unexpected test results. When a test result is different than predicted, a review of how the new result impacts safety practices must be made;

6. where members of the laboratory staff become ill, suspect exposure, smell chemicals, or otherwise suspect a failure of engineered safeguards.

Any new procedures should be subjected to peer review. Not only from a scientific standpoint, but also to assure that all safety considerations are in place prior to implementation.
### Part IX. Medical Surveillance and Record Keeping

Any researchers or employees in the lab setting with concerns for potential risk from chemical or physical agents may contact Occupational health Services at 777-3472 or 777-0761. Any individual who believes they may have been exposed to a hazardous substance (see Part VI.A), either through routine exposure or during an accident or spill, should notify their supervisor immediately and contact Occupational Health Services. Individuals who experience any adverse health effects from exposure to hazardous substances should immediately report to Occupational Health Services (Thomson Student Health Center, room 303, phone 777-3472). Emergency assistance can be obtained by calling extension 7-9111 (on-campus) or 777-9111 (off-campus). All accidents involving exposure to hazardous substances that require medical attention must be reported in writing to the laboratory supervisor and the Chemistry Department Chemical Hygiene Officer (Professor Stephen L. Morgan, phone 777-2461).

Special programs of ongoing medical surveillance are available for researchers planning extended work with certain hazardous substances. Enrollment in these programs can be arranged by calling Occupational Health Services at 777-3472. There are no charges for these services. Typical hazardous substances and classes of substances for which medical surveillance may be advisable include:

asbestos	carcinogens	arsenic	beryllium
lead	mercury	cadmium	thallium

It is the responsibility of the laboratory supervisor to identify workers in their group who will be engaged in research that may involve hazardous exposures requiring medical surveillance. When indicated, medical surveillance may include a physical exam by a licensed physician; contact Occupational Health Services (777-3472). The examining physician will then provide a written opinion including:

(a) any recommendation for further medical follow-up;

(b) the results of the examination and any associated tests;

(c) any medical condition(s) revealed in the course of the examination which may place the employee at increased risk; and

(d) a statement that the employee has been informed by the physician of the examination results and any medical condition requiring further examination or treatment.

The written opinion will not reveal findings unrelated to the occupational exposure.

Record keeping shall be conducted as follows:

(a) Health & Safety Programs Unit shall establish and maintain an accurate record of exposure measurements when an exposure has been assessed quantitatively for various chemical and physical agents. Any medical consultations/examinations including tests or written opinions required by 29 CFR 1910.20, *et al.*, are maintained by Occupational Health Services.

(b) Occupational Health Services shall assure that such records are kept, transferred, and made available to employees in accordance with 29 CFR 1910.20.

## Part X. Accidents and Emergencies

#### **A. Emergency Procedures**

Call the Campus Police 24 hour line 7-9111 (777-9111 off-campus phones) to obtain assistance in the event of an emergency. Report the nature and location of the emergency, including both your building and floor number.

Notify other workers in the area of the nature of the emergency. If necessary, activate the fire alarm to order the evacuation of the building. When the fire alarm sounds, all personnel, without exception, are required to leave the building.

Procedures for handling the accidental release of hazardous substances are discussed in Part VI.C.12.

Procedures to follow in the event of a fire are discussed in Part VI.D.

If a coworker has ingested a toxic substance, have the person drink one glass of water and call the Poison Control Center immediately ((765-7359, 24 hours a day, 7 days a week). Never give anything by mouth to an unconscious person. Attempt to learn exactly what substances were ingested and inform the medical staff as soon as possible.

If a coworker is bleeding severely, immediately put on water-proof gloves (which should be readily available), elevate the wound above the level of the heart and apply firm pressure directly over the wound with a clean cloth, handkerchief, or your gloved hand. Obtain immediate medical assistance.

7. Do not touch a person in contact with a live electrical circuit—disconnect the power first!

#### **B.** Medical and First Aid Information

Medical and first aid requirements are stated in OSHA 191.151 (see Part XIII).

1. Every laboratory should provide basic first aid supplies in a readily accessible location, maintained in a clean and hygienic manner. Occupational Health Services will facilitate the purchase of first aid kits by recommending basic first aid supplies. Covering the cost of such kits is the responsibility of the individual laboratory.

2. Two persons certified (American Red Cross, OSHA approved) in basic first aid must be available on each shift. First aid training is available from the Health & Safety Programs Unit (777-5269).

3. Emergency phone numbers must be posted in a highly visible location and updated when necessary. The "Emergency Phone Numbers for University Services" included in this Chemical Hygiene Plan (see page 2) is designed to be copied and posted by laboratory telephones.

4. Any necessary medical directives should be signed by the consulting physician and updated on a annual basis by Occupational Health Services.

#### C. Laboratory Emergency Information Signs

Every laboratory door should be posted with an up-to-date yellow emergency information sign that lists the names of key personnel working in the laboratory and information (*i.e.*, telephone numbers) on how to reach them in the event of an emergency. It is the responsibility of laboratory supervisors (with the assistance of group safety officers) to ensure that these signs are updated regularly. If you need to have an Information Sign posted on your laboratory, contact the Chemical Hygiene Officer.

#### **D. Accident Reports**

To help identify and correct unexpected hazards ad to prevent future accidents, it is necessary that personnel prepare **written** reports describing the circumstances of all serious accidents or all incidents that might have resulted in a serious accident.

One copy of the report should be submitted to the Department Chemical Hygiene Officer (Professor Stephen L. Morgan, GSRC 208, 777-2461), and one copy should be given to the supervisor of the laboratory in which the accident took place. Reports should be filed within a week of the date of the accident.

Written accident reports must be prepared using the form on the next page following any of the following incidents:

- 1. Fires that require the use of a fire extinguisher or require sounding a fire alarm.
- 2. Any accident that results in an injury requiring medical attention.
- 3. Any **spill** of a hazardous substance that takes place outside a designated area. Any accidental release of a *Particularly Hazardous Substance* requires the filing of an accident report.

The investigation of accidents is done not to assign blame to individuals but to reveal the factual circumstances related to the accident. Accident investigations are conducted by the Chemical Hygiene Officer in collaboration with USC Health & Safety Programs unit. The incident scene should be examined before the physical evidence is disturbed, cleaned up, or removed. Unknown spills or residues will be sampled. Blueprints, circuit diagrams, or other relevant documents will be reviewed if needed. Employees involved in the accident and other witnesses will be interviewed and asked to provide written reports. Conditions or circumstances deviating from normal will be noted. All hypotheses of cause will be listed. Based on the review of the incident, past operating experience, and employee recommendations, the proximate cause of the accident will be determined. Finally, corrective and preventive action will be recommended. Suggestions will be made for correction of the investigation all concerned individuals should avoid unwarranted conclusions that create a false impression of certainty, statements that can be interpreted as opinions of legal position or liability with respect to the incident, and unnecessary discussion of rumors as the accident report is being prepared.

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

#### E. Accident Report Form

See page 12.

### Part XI. Glossary of terms and symbols

ACGIH American Conference of Government Industrial Hygienists. Publishes "TLV's, Threshold Limit Values for Chemical Substances in Workroom Air Adopted by ACGIH for 1979," ACGIH, Cincinnati, OH, 1979.

Acute An adverse effect or injury to health that occurs immediately or shortly after a single or short term exposure to a material or condition.

Cancer Uncontrolled tissue growth resulting in formation of malignant tumors.

Carcinogen A substance capable of causing cancer.

CFR Code of Federal Registry.

Chronic An adverse effect, injury, or illness with symptoms that develop after long term exposure to a material or condition.

Combustible Able to catch fire and burn.

**Corrosive chemicals** Chemicals that are capable of causing damage to skin, eyes and respiratory epithelium by contact with the chemicals or its vapors.

Developmental hazard An agent that interferes with the development of an individual before or after birth.

Embryotoxic A substance that is poisonous to the unborn organism or fetus.

Environmental monitoring The measuring of concentrations of airborne hazardous substances.

Flammable Capable of being easily ignited and of burning.

**Highly toxic** A chemical that has an:  $LD_{50}$  by ingestion of more than 50 mg/Kg or less;  $LD_{50}$  by contact of more than 200 mg/Kg or less;  $LC_{50}$  by inhalation of 200 ppm or less, or 2 mg/liter or less.

Irritant A chemical that causes a reversible inflammatory effect on living tissues by chemical action at the site of contact.

Laboratory A work place where relatively small quantities of chemicals are being used on a non-production basis.

Laboratory Scale Work with chemicals that can easily and safely manipulated by one person.

LC<sub>50</sub> (Lethal Concentration 50%) The concentration of a substance that causes death in 50% of the animals exposed.

LD<sub>50</sub> (Lethal Dose 50%) The dose that causes death in 50% of the animals exposed.

MSDS Material Safety Data Sheet

Mutagen A substance capable of changing cells in such a way that future cells generated are affected.

NEC National Electrical Code.

NFPA National Fire Protection Association

**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 allowable concentration in the work place that is considered a safe level of exposure for eight hour shift, 40 hours per week.

pH A measure of how acidic or basic a substances is on a scale of 1 being the most acidic to 14 being the most basic.

Sensitizers Agents that can cause an allergic reaction with repeated exposure over time.

Sterility Changes made in male or female reproductive systems resulting in the inability to reproduce.

Teratogen A substance that causes a deformity in fetal growth if significant exposure exist during pregnancy.

**TLV or TWA** Threshold Limit Value or Time Weighed Average. The amount of exposure allowable for an employee in an eight hour work day.

### Part XII. REFERENCES

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Notes

# Part XIII. OSHA LAB STANDARD 29 CFR 1910.1450

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