Department of Chemistry
Safety Manual

October 2018

Safety Committee
Department of Chemistry
Hong Kong University of Science and Technology

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This safety manual is written in English. It is your responsibility to ensure that you understand completely the meaning and portent of what is described herein. Further, you must ensure that you understand spoken commands issued in English as these pertain to safety issues, particularly with regard to ***any*** *emergency procedure.*

HKUST policy requires that all personnel, including visitors, wear eye protection at all times while in Chemistry Department experimental laboratories. Not to do so may incur disciplinary action. Eye protection is discussed in detail in Chapter 4.1 of this Safety Manual.

Whenever chemical waste is added to a chemical waste container, immediately enter the information of the new waste to the chemical waste log sheet attached to the container.

Whenever equipment or apparatus is to be used, irrespective of its complexity, it is your responsibility to ensure that you understand fully its operation, and all emergency procedures in the event of equipment failure. An equipment malfunction due to improper use arising as a result of lack of knowledge of the equipment, or carelessness, amounts to academic misconduct, and will be treated as such. This also applies if there is a fire, flood or other incident arising as a result of improper use of equipment.

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1.0 Introduction

Preamble

The Occupational Health and Safety Ordinance (OHSO) passed by the Hong Kong Government in 1997 stresses the importance of a safety management programme which integrates all aspects of work place safety with line management and responsibility of individuals engaged in any operation involving chemicals, machinery, or energy source.

According to the University Health, Safety and Environment Office (HSEO), effective department safety management incorporates the following elements:

1. *Accountability*:
   Department heads are accountable for the safety performance of their staff and employees and for the safe conduct of tasks in the department. HSEO provides assistance to help departments in achieving this goal.

2. *Clear statement of safety policy and procedures*:
   Each department must have a safety policy in line with the University's general safety policy, and which contains procedures which address operations specific to the department.

3. *Departmental Safety Officer*:
   The department must have a faculty member as the Safety Officer for the department. The appointee carries the department head's authority in implementing safety. Other faculty members, technical staff and student members assist the Safety Officer in implementing safety measures.

4. *Departmental Safety Committee*
   The department must have a safety committee to address safety issues within the department, to monitor safety performance including performing safety inspections and to assist HSEO with the formulation of safety policies within the department. In conjunction with HSEO, this Committee must review accident statistics and take the appropriate corrective actions.

5. *Safety Performance Evaluation*
   Safety is emphasized as an integral part of any job. It is as important to do a job correctly as to do it safely. Employees are held accountable to follow safety procedures in doing the job. As part of an employee's performance appraisal, safety compliance needs to be one of the elements to be considered.

6. *Responsibility of Faculty Members in Ensuring Safety*
   Safety is a line responsibility. Faculty members are responsible for ensuring that their employees and students are aware of the potential hazards associated with their operations. They and the personnel under their supervision must be familiar with the required safety controls and emergency procedures.

7. *Responsibility of Faculty Members in Ensuring Job Specific Safety Training*
   While HSEO provides a number of general safety courses, supervisors are responsible for adopting guidelines stated in HSEO's general safety courses, to address specific operations in their own laboratories. This on-the-job training should include specific methods for handling specific hazardous agents used in the particular laboratory as well as the specific emergency response procedures appropriate for that laboratory. Supervisors are responsible for conducting job-specific safety training.

8. *Regular Laboratory Inspections*
   Safety inspections should be conducted as a joint effort involving all personnel for promotion and safety assurance. Supervisors are required to perform periodic safety inspections of their own laboratories to monitor for compliance with established safety procedures. In addition, the departmental Safety Committee and HSEO conduct announced and unannounced safety inspections of laboratories to provide feedback to management on safety performance.

9. *The Provision for Work Stoppage in Case of Doubt*
   Employees and students are required to consult their supervisors if they feel unsure of the operation. Supervisors should monitor the performance of students and employees and take positive action including stopping work, where necessary, when hazardous situations are spotted. HSEO has the authority to stop operation when any imminently dangerous situation is observed or when repeated safety violations occur.

10. *Departmental Liaison and Cooperation with HSEO*
    HSEO holds regular meetings with department heads to evaluate safety performance, compliance issues, accident data and inspection findings. HSEO provides consultation and services to help faculty members in implementing safety measures. These services include facility and operational planning, laboratory inspections and audits, general safety training, exposure assessment, medical surveillance, *etc*. Departmental management must co-operate with HSEO in addressing safety concerns.

The Department of Chemistry Safety Manual

The *Department of Chemistry Safety Manual*, compiled by the Safety Committee of the Department of Chemistry of the Hong Kong University of Science and Technology (HKUST), is designed to provide specific guidelines and recommendations for confronting the unique hazards present in chemical research laboratories, in line with the above precepts. It complements the *Safety and Environmental Protection Manual* issued by the Safety and Environmental Protection Office (HSEO) of HKUST.

This manual incorporates the concept of a "Chemical Hygiene Plan," a laboratory safety and health standard designed to protect laboratory workers from chemical hazards in the workplace. This standard (29 CFR 1910.1450) was developed by the Occupational Safety and Health Administration (OSHA) of the United States of America.

The United States Federal Register (Vol. 55, No. 21, Wednesday, January 31, 1990, p. 3327-3335) defines a "Chemical Hygiene Plan" as a

> "written program developed and implemented by the employer which sets forth procedures, equipment, personal protective equipment, and work practices that are capable of protecting employees from the health hazards presented by hazardous chemicals used in that particular workplace…"

The full text of standard 29 CFR 1910.1450 is available from the Chairman of the Chemistry Safety Committee.

The standard became effective May 1, 1990, and all laboratories in the United States were required to have such a plan by January 1, 1991. The Chemistry Department of HKUST, though not bound by Hong Kong Law to have any such "Chemical Hygiene Plan," nevertheless has decided to follow the general guidelines laid out in 29 CFR 1910.1450.

2.0 Safety Policy and Responsibility for Safety

Department of Chemistry's Safety Policy:

It is the policy of HKUST to assume all reasonably practicable directives to protect its appointees, students, facilities, and the environment. And Department of Chemistry shares the same commitment of the University.

Faculties and laboratory managers are responsible for ensuring that their employees and students are aware of the potential hazards associated with their operations.

Employees and students should take appropriate safety precaution to avoid injuries to themselves, other members of the University or of the community. In case of query, employees and students should stop their operation and seek advice from their supervisor or from HSEO.

All members in the Department of Chemistry should implement the applicable policies and procedures written in the HKUST safety manual and in the Departmental safety manual.

Safety is everyone's responsibility. All activities must be planned carefully to ensure a safe working environment and to comply with the University and statutory regulations. Safety is not the sole responsibility of a single organization or individual—everyone must play their role to ensure a safe working environment. Within the Department safety responsibilities are organized in the following way:

2.1 Department Head

The Department Head has ultimate responsibility for safety in the Department. The Department Head

- appoints the members of the Chemistry Department Safety Committee, to manage safety issues in the department.
- provides the necessary personnel and financial support for the work of the Committee.
- enforces compliance with University and Departmental safety policies and procedures.

2.2 Department of Chemistry Safety Committee

2.2.1 Charter of the Department of Chemistry Safety Committee (10/95)

Terms of Reference

1. In consultation with HSEO, to establish and oversee safety policies for the Department of Chemistry.
2. In consultation with HSEO, to prepare and update the Departmental Safety Manual
3. To establish and oversee administrative procedures designed to ensure that all faculty, staff, and students receive adequate training to perform laboratory work safely.
4. To conduct quarterly safety inspections of the laboratories.
5. To act as a liaison between the Department and HSEO.

Membership

1. At least three academic faculty members, appointed by the Department Head.
2. One representative at Tech/Sr. Tech rank, appointed by the Department Head, to serve as Deputy Fire and Safety Officer (Deputy FSO).
3. One postgraduate student member, appointed by the Chair of the Committee.

Chair/Departmental Fire and Safety Officer:

The Committee is chaired by one of the academic faculty members, who is appointed by the Head of Department. The Chair will assume the role of Fire and Safety Officer (FSO) (required by HSEO for each Department), and will carry the authority of the Head in dealing with Departmental Safety matters.

Term:

One year, renewable.

2.2.2 Current Membership of Safety Committee (2018-present):

Professor Rongbiao TONG (Chair of Fire and Safety Officer)
Professor Zhihong GUO
Professor Jonathan HALPERT
Dr. Enrique KWAN (Departmental Safety Officer)
Mr. Disney Chun Tak LAU (Technician and Deputy DSO)
Ms. Amy HO (General Office)

2.3 Laboratory Supervisor (Principal Investigator)

Each faculty member is directly responsible for:

- compliance of the members of his/her group with Departmental and University safety policies and procedures.
- providing "hands-on" instruction on how to perform hazardous operations (i.e. "job-specific" safety training).
- developing written plans (Operational Safety Procedures, "OSPs") describing how to safely perform common operations in their laboratories that involve the use of certain hazardous chemicals or equipment.
- ensuring a safe work environment in his/her lab by identifying and mitigating potential hazards.

2.4 Researchers

Researchers are responsible for:

- completing the safety training required by the Department.
- compliance with the safety policies and procedures of the Department and University.
- proper planning and risk assessment of their experimental work (when uncertain, researchers are responsible for contacting their supervisors for assistance).

2.5 Safety and Environmental Protection Office (HSEO)

HSEO performs the following functions:

- provides direct liaison between Hong Kong Government Labour Department Occupational Health and Safety Ordinance (OHSO) and the University over matters of procedure and implementation.
- assists in setting safety policies and procedures.
- assists in facility and operational planning to address safety concerns.
- advises on safety measures and the selection of appropriate personal protective equipment.
- provides general safety training.
- conducts periodic announced and unannounced safety inspections and audits.
- monitors exposure to hazardous materials and assesses environmental parameters to ensure compliance.
- stops operations which are imminently dangerous or involve repeated safety violations.
- supplies unit heads with monthly accident and incident summaries.
- provides feedback on safety performance to unit heads for follow-up action.

3.0 Information, Training, Safety Clearance, and Safety Clearance at Graduation/Termination

3.1 Initial Training

All members of the Chemistry Department should be familiar with the hazards associated with the chemicals and equipment present in their work area. To ensure that researchers receive the safety information they need to protect themselves, the Department has put in place the following administrative controls.

1. Safety Clearance Form

The Departmental Safety Clearance Form is form is reproduced in Appendix I of this manual

New personnel must complete parts A-C of the Departmental Safety Clearance Form from Amy Ho and return it to the Department Office *before starting any laboratory work*, or within two weeks of assuming duty, whichever is sooner. *Faculty supervisors are responsible* for ensuring that a new appointee receives this form and completes it within the specified time frame.

The commitment of both the supervisor and the appointee to understanding of chemical and physical health hazards must be noted.

The requirement of completing the Departmental Safety Clearance Form applies to all, regardless of rank (from Undergraduate Researcher to Professor), and regardless of the length of appointment. In the case of very short term visitors (less than two weeks) the Chairman of the Safety Committee should be consulted for assistance in completing the Safety Clearance Form.

Part A and **Part B** of this form require that new personnel:

- Register for the two required HSEO Courses [*Chemical Safety for Laboratory Users* (MC 07), and *Hazardous Waste Management* (MC 03)]
- Obtain a pair of Safety Glasses from the Deputy Departmental Safety Officer and if necessary complete a request form for order of Prescription Safety Glasses.
- Read specified portions this Safety Manual and the University *Safety and Environmental Protection Manual*.
- Receive a Basic Lab Safety Orientation from their supervisor to learn the location and proper use of the safety equipment in their laboratory and its surroundings.

Part C of this form requires supervisors to specify whether the new appointees will need to undergo additional safety training courses from HSEO (e.g. *Laser Safety*, *Safety with Gas Cylinders*, *Safe Handling of Irradiating Apparatus and Sealed Sources*, *Respiratory Protection*, *Fire Extinguisher Training*, etc.)

If on the other hand a supervisor can certify that a new appointee will never perform or supervise experimental work, he/she should sign the "Waiver for Theoreticians" on the *Safety Clearance Form* and the appointee will then be exempt from completing the Form.

New PG students will generally not begin laboratory work or choose a research supervisor within two weeks of assuming duty. In any event, the student must first complete Part A, return the form to the office (by the two week deadline), and then subsequently complete parts B-C *before starting laboratory work*.

2. **Faculty Supervision:**
   Until the new appointee has completed the required HSEO safety training, he/she must work under the direct supervision of his/her supervisor.

3. **Record Keeping:**
   The Department general office maintains a database summary of the Safety Clearance Forms, and periodically runs checks to determine which personnel have not fulfilled their requirements.

The hazards present in the laboratories of the Chemistry Department vary widely from group to group, and consequently it is the *responsibility of both the supervisor* ***and*** *the personnel* to ensure that they have received *all* proper information and training on the specific hazardous chemicals used in the individual group.

Laboratory course TAs are required to attend the special safety training session held for undergraduate students enrolled in chemistry laboratory courses at the beginning of each semester.

Each supervisor should also conduct periodic oral examinations to monitor the familiarity of research personnel with specific issues, such as knowledge of hazardous properties of chemicals, and of the provisions of the Safety Manual. Appendix IV of this plan includes a list of sample safety questions that should be relevant to most work involving hazardous substances in the department.

In addition, in conjunction with HSEO, a regular three-monthly review is conducted to assess workplace hazards evaluation in the specific laboratory. A summary sheet 'HKUST Workplace Evaluation Sheet' is prepared, and displayed in a prominent place within the laboratory. All personnel are required to be familiar with the hazards in their work area. Individual supervisors are also encouraged to write and disseminate safety rules known as "Operational Safety Procedures" (OSPs) to govern use of specific equipment in their laboratory. Certain activities mandate the writing of an OSP. These are described in Chapter 7.6 "Operational Safety Procedures" of this Manual.

3.2 Information on Hazardous Substances

It is a compulsory requirement of the Departmental Safety Committee that all researchers be familiar with the health and physical hazards of *all* chemicals involved in their work. Operators shown not to be aware of these properties may not be permitted to commence or to continue an experiment.

1. Hard copy format

Information in hard copy format on hazardous chemicals and procedures for handling them can be obtained from books available in the Chemistry Department Safety Library (Rm. 7127, the "Tea Room"), the University Library and the HKUST HSEO

Office (Rm. 2005, Lift 4, ext. 6512). Material Safety Data Sheets (see below) are another valuable source of information.

Books available in the Chemistry Department Safety Library (Rm. 7127):

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

CRC Handbook of Laboratory Safety (4th edition), A. K. Furr, Ed., 1995 (a 783 page reference on all aspects of lab safety).

Destruction of Hazardous Chemicals in the Laboratory, G. Lunn and E. B. Sansone, 2nd Ed., 1994 (detailed procedures for destruction of hazardous substances via chemical reactions).

Prudent Practices for Disposal of Chemicals from Laboratories, prepared by the National Research Council, 1983 (282 pages).

Prudent Practices for Handling Hazardous Chemicals in Laboratories, prepared by the National Research Council, 1981 (291 pages).

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

NIOSH Pocket Guide to Chemical Hazards, U.S. Department of Health and Human Services, Public Health Service, Centers for Disease control and Prevention, National Institute for Occupational Safety and Health, June 1997 (handbook providing chemical name, synonym, recommended exposure limits (REL), personal protection, health hazards for 677 chemicals or substance groupings).

1999 Threshold Limit Values and Biological Exposure Indices for Chemical Substances and Physical Agents, American Conference of Governmental Industrial Hygienists, 1999 (TLVs and BEIs for chemical substances, and TLVs for physical agents – sound, radiation, heat *etc.* in the work environment).

Guide to Occupational Exposure Values – 1998, compiled by the American Conference of Governmental Industrial Hygienists, 1998 (TLVs, PELs, RELs, maximum concentration values at workplace of over 1000 chemical substances).

In the University Library

Handbook of Reactive Chemical Hazards Fifth Edition, L. Bretherick, 1995 (the best compilation of information on the hazards of reactive and explosive materials. Information on the stability, explosibility, and incompatibilities of over 9,000 compounds is included). T55.3.H3 B73 1995 v.1-2.

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

CLS routinely provides end-users with MSDS's when a chemical is ordered from CHEMSTOCK. However, MSDS's are not provided for chemicals ordered directly from outside suppliers. Users can easily obtain MSDS's for these items by connecting to the Library Online System (PC only) (see below).

2. Soft Copy format

Information on hazardous chemicals in soft-copy format (on-line) may be obtained from the HSEO Web Page, which also provides links to overseas compendia listing chemical hazards, and occupational exposure values.

HSEO Web Page (http://www.ab.ust.hk/sepo.html)

A comprehensive CD-ROM database entitled Sigma-Aldrich MSDS is available. This includes three databanks containing information on potentially hazardous chemicals. MSDS (Material Safety Data Sheets) and CHEMINFO profile over 90,000 chemicals with evaluations of health, fire and reactivity hazards, as well as recommendations on handling and storage, disposal procedures, accidental release, and first aid. RTECS (Registry of Toxic Effects of Chemical Substances) holds chemical identification and toxicity data on over 130,000 chemicals. It also includes three bibliographic databases, DIDS, HSELINE, and NIOSHTIC providing nearly 400,000 citations and abstracts to literature on occupational health and safety.

Procedure for connecting to Sigma-Aldrich MSDS CD-ROM over the HKUST network

Access: Only through the Windows 98 version of the Library Online System

i Choose "Library Online Systems"
ii Choose "Online Databases"
iii Choose "Complete List of Databases"
iv Choose "Science"
v Choose "Sigma-Aldrich MSDS"

You may then search for a particular MSDS by the chemical name, CAS Registry Number, formula, chemical family, name fragment.

3.3 Additional Safety Information

A copy of the Safety and Environmental Protection Manual, published by HSEO, provides information on wide range of subjects, including chemical safety. Each laboratory is required to have a copy of this manual. In addition, you may browse or search the HSEO manual online (PC Only):

Procedure for Browsing or Searching the HSEO Manual Online:

i. Browse HSEO webpage (http://www.ab.ust.hk/sepo/index.html)
ii. Choose "Publications"
iii. Choose "Safety & Environmental Protection Manual"

3.4. Safety Clearance at Termination

All personnel who have been engaged in research must complete a safety clearance *before* they leave the University. This is to ensure that departing personnel do not leave behind hazardous materials or experimental set-up, and to document their occupational health condition when they leave HKUST.

Procedure for M.Phil. and Ph.D. students

i. The HKUST Student Safety Clearance at Graduation Form (Appendix II) is to be filled out *at the same time* as the 'Notice of Intention to Take Thesis Examination'. The University requires that the student submit *both* forms to the Departmental secretariat about four weeks prior to the thesis examination.
ii. The Department sends the completed form to HSEO *two weeks* before the student leaves HKUST.
iii. The University Office for Academic Affairs will copy the Notice of Intention to Take Thesis Examination for to HSEO. HSEO will then inform the Department if Safety Clearance is granted.
iv. *Failure to complete the Safety Clearance requirements will be considered as a failure to complete graduation requirements*.

Procedure for M.Sc. students

Whether a Safety Clearance at Graduation is required by M.Sc. students depends upon the nature of their research work. If laboratory work is involved, then the student must go through safety clearance.

Procedure for Staff

i. The HKUST Staff Safety Clearance at Termination Form (Appendix III) must be filled, signed by the supervisor and the Head of Department, *no later* than two weeks prior to the staff member leaving the University.
ii. The Department sends the completed form to HSEO.
iii. HSEO will clear with the Department of all safety issues and inform Personnel Office that the staff member has no remaining safety obligations to HKUST.

4.0 Personal Protective Equipment and Safety Engineering Controls

This section of the Safety Manual discusses equipment and personal apparel that may be required to protect researchers from the hazards presented by certain chemicals. Note that work with specific hazardous substances often require the use of special protective equipment. See Chapter 5 of this Manual for further discussion of work situations that require the use of protective equipment and/or the MSDS for the specific chemical in use.

4.1. Eye Protection

HKUST Chemistry Department policy requires that all personnel, including visitors, wear eye protection at all times while in Chemistry Department laboratories. Not to do so is rated an offence, and disciplinary action may be incurred.

Eye protection is required whether or not one is actually performing a "chemical operation". Visitors should not be permitted to enter a lab unless they wear appropriate eye protection. Accidents by definition occur unexpectedly. You must be prepared for hazards arising from the work of others. Groups that handle chemicals are advised to have a supply of safety glasses for the use of visitors.

Ordinary prescription glasses do not provide adequate protection against injury, and therefore do not constitute adequate eye protection.

Therefore the minimum acceptable standard for eye protection is either
1. Safety Glasses (non-corrective) with side shields (available from the Deputy FSO).
2. Prescription Safety Glasses with side shields (see below).

Those needing corrective lenses who have not yet received their prescription safety glasses must wear Safety Glasses or Goggles over their normal corrective lenses.

Note that Safety Glasses are designed primarily for impact protection and do not provide adequate protection against splashing of hazardous liquids. Only Goggles are effective against this kind of splash hazard (see below).

Safety glasses must meet the American National Standards Institute standard Z87.1-1989 which specifies a minimum lens thickness (3mm), certain impact resistance requirements, *etc*. Any doubt about whether a particular pair of glasses meets this specification is easily resolved by ascertaining whether the code "Z87" inscribed on the edge of the lense or frame. Although these safety glasses can provide satisfactory protection against injury from flying particles, they do not fit tightly against the face and offer little protection against splashes or sprays of chemicals. Other eye protection should therefore be employed whenever a significant splash hazard exists (see below).

It is HSEO policy to provide prescription safety glasses free of charge to all those personnel working in laboratories who must wear glasses to correct their vision. To obtain prescription safety glasses at HKUST's expense, you must fill out the Order form (available from Ms. Amy Ho in the Departmental Office), and have it signed by your supervisor. To place your order, you should then forward the form to the HSEO Office.

Contact lenses offer no protection against eye injury and cannot be substituted for safety glasses and goggles. Contact lenses should not be worn when carrying out operations where a chemical splash to the eyes is possible since contact lenses interfere with first aid and eye-flushing procedures. *Thus, the wearing of contact lenses in the laboratory is expressly* *forbidden.* Only when an individual can produce certified documentation to the Chairman of the Safety Committee that he/she must wear contact lenses for medical reasons can an exception be made. In such a case tight-fitting goggles must be worn over the contact lenses.

Goggles should be worn when carrying out operations in which there is a reasonable chance of splashing chemicals, flying particles, etc. For example, goggles are preferred over regular safety glasses when pouring large quantities of hazardous liquids, 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 no protection to the neck, *full-face shields* should be worn when conducting particularly hazardous laboratory operations. In addition, the use of laser or ultraviolet light sources requires special glasses or goggles which have been approved by the HSEO.

4.2. Protective Apparel

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

1. Skin contact with *any* chemical must always be avoided. Any mixture of chemicals should be assumed to be more toxic than its most toxic component, and substances whose hazards have not been evaluated should be treated as hazardous.
2. As will be discussed in Chapters 5 and 6, work with certain chemicals and classes of chemicals requires that protective apparel such as a lab coat or chemical-resistant apron be worn. Lab coats are available from the Deputy FSO.
3. Sandals or open toed shoes are not allowed and long hair and loose clothing should be confined when present in the laboratory. More stringent rules may apply when working with hazardous substances (see Chapter 5.2).
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 (at the relevant concentration). 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. *and entering data into laboratory note books*

Note that not all gloves are suitable for all purposes. The following table should be consulted in the selection of proper gloves for a given task.

Table 1. Glove Selection Table. Chemical Resistance is rated as: E = Excellent, G = Good, F = Fair, P = Poor

Chemical	Natural Rubber	Neoprene	Nitrile	Vinyl
Acetaldehyde	G	G	E	G
Acetic acid	E	E	E	E
Acetone	G	G	G	F
Acrylonitrile	P	G	-	F
Ammonium hydroxide (sat)	G	E	E	E
Aniline	F	G	E	G
Benzaldehyde	F	F	E	G
Benzene [1]	P	F	G	F
Benzyl Chloride [1]	F	P	G	P
Bromine	G	G	-	G
Butane	P	E	-	P
Butyraldehyde	P	G	-	G
Calcium hypochlorite	P	G	G	G
Carbon disulfide	P	P	G	F
Carbon tetrachloride [1]	P	F	G	F
Chlorine	G	G	-	G
Chloroacetone	F	E	-	P
Chloroform [1]	P	F	G	P
Chromic acid	P	F	F	E
Cyclohexane	F	E	-	P
Dibutyl ether	F	G	-	P
Dibutyl phthalate	F	G	-	P
Diethanolamine	F	E	-	E
Diethyl ether	F	G	E	P
Dimethyl sulfoxide [2]	-	-	-	-
Ethyl acetate	F	G	G	F
Ethylene dichloride [1]	P	F	G	P
Ethylene glycol	G	G	E	E
Ethylene trichloride [1]	P	P	-	P
Fluorine	G	G	-	G
Formaldehyde	G	E	E	E
Formic acid	G	E	E	E
Glycerol	G	G	E	E
Hexane	P	E	-	P
Hydrobromic acid (40%)	G	E	-	E
Hydrochloric acid (conc)	G	G	G	E
Hydrofluoric acid (30%)	G	G	G	E
Hydrogen peroxide	G	G	G	E
Iodine	G	G	-	G
Methylamine	G	G	E	E
Methyl cellusolve	F	E	-	P
Methyl chloride [1]	P	E	-	P
Methylene chloride [1]	F	F	G	F
Methyl ethyl ketone	F	G	G	P
Monoethanolamine	F	E	-	E
Morpholine	F	E	-	E
Naphthalene [1]	G	G	E	G
Nitric acid (conc)	P	P	P	G
Perchloric acid	F	G	F	E
Phenol	G	E	-	E
Phosphoric acid	G	E	-	E
Potassium hydroxide (sat)	G	G	G	E
Propylene dichloride	P	F	-	P
Sodium hydroxide	G	G	G	E
Sodium hypochlorite	G	P	F	G
Sulfuric acid (conc)	G	G	F	G
Toluene [1]	P	F	G	F
Trichloroethylene [1]	P	F	G	F
Tricresyl phosphate	P	F	-	F
Triethanolamine	F	E	E	E
Trinitrotoluene	P	E	-	P

[1]Aromatic and halogenated hydrocarbons will attack all types of natural and synthetic glove materials. Should swelling occur, the user should change to fresh gloves and allow the swollen gloves to dry and return to normal
[2] No data on the resistance to dimethyl sulfoxide of natural rubber, neoprene, nitrile rubber, or vinyl materials is available: the manufacturer of the substance recommends the use of butyl rubber gloves.

(Table taken from *Prudent Practices for Handling Chemicals in the Laboratory*, National Research Council, National Academy Press, Washington DC, p. 159-160, 1981)

It is worth noting that the green nitrile rubber gloves commonly used in our Department offer "excellent" or "good" protection against most chemicals *except for oxidizing acids*. When handling these materials vinyl rubber gloves are preferred. Finally, the above table does not contain data on the performance of nitrile rubber gloves against halogens and hydrocarbons.

It is also important to point out that natural rubber gloves (e.g. "latex" gloves) offer only fair to poor protection against common laboratory solvents, and thus should not be worn when dispensing solvent or rinsing glassware with acetone.

4.3 Respirators

It is the University's goal to control respiratory hazards at their point of generation by using engineering controls and good work practices. In keeping with this goal, the use of respirators as the primary means of protecting employees from airborne hazards is considered acceptable only in very specific situations. These situations include short-term temporary experiments where engineering controls are not feasible, and situations in which the use of respiratory protection is an added or supplemental control. The following guidelines must be followed when using respirators:

1. Before anyone can wear a respirator, conditions must be met as discussed below with respect to (a) training, (b) medical approval, and (c) fit testing.
2. Personnel must participate in a Respiratory Training Course prior to using a respiratory device. This training is provided by HSEO and includes discussion of the proper use, maintenance, testing, cleaning, and storage of respiratory equipment.
3. HSEO regulations require a medical evaluation of all personnel intending to use a respirator. Appointments for medical evaluations are arranged after successful completion of the above course.
4. The type of respirator to be used will be selected in consultation with HSEO. Respirators can only be obtained with HSEO approval, and are assigned to individuals for their exclusive use.
5. All users must undergo fit testing (conducted by HSEO) when a respirator is issued.
6. HSEO will maintain records of respirator users.

4.4 Laboratory Fume Cupboards

Local exhaust ventilation is the primary method used to control inhalation exposures to hazardous substances. The laboratory fume cupboard is the most common local exhaust method used in the Chemistry Department. Other types of local exhaust include vented enclosures for gas cylinders, large pieces of equipment or chemical storage, and snorkel ("elephant trunk") types of exhaust for capturing contaminants near the point of release. Local exhaust systems consist of some type of fume cupboard, duct work, and fan located on the roof. Some systems are equipped with air cleaning devices (HEPA filters or carbon adsorbers). In most cases one fan services 3-4 fume cupboards.

It is necessary to use a laboratory fume cupboard whenever hazardous substances or "particularly hazardous substances" (see Chapter 6) are in use. In some special cases another suitable type of containment device (such as those listed above) can be used providing that it has been certified effective by HSEO. A properly operating and correctly used laboratory fume cupboard can control the vapors released from volatile liquids, as well as dust and mists.

Any physical modifications to fume cupboards or duct work can only be done by FMO (facilities management office, laboratory service section, Albert Chan, ext. 6880) or the University's approved contractor.

Do not use a laboratory fume cupboard for large pieces of equipment unless the fume cupboard is dedicated to this use (large obstructions can change the airflow patterns and render the fume cupboard unsafe for other uses). It is generally more effective to install a specifically designed enclosure for large equipment so that the laboratory fume cupboard can be used for its intended purpose.

Fume Cupboard Certification:

HSEO annually inspects all laboratory fume cupboards in the Chemistry Department. This inspection consists of measuring the face velocity of the fume cupboard. If the laboratory fume cupboard passes the certification test, then an updated certification label is affixed to the fume cupboard. If the fume cupboard does not pass inspection then it is considered unsafe for use, and will be labeled with a "DO NOT USE" sign.

If a fume cupboard fails inspection due to a mechanical problem, a defect report should be filed with OLS, and upon completion of the repair work the fume cupboard is then re-inspected. If a fume cupboard functions poorly due to incorrect use (e.g. cluttered fume cupboards) then HSEO will notify the Department Safety Committee Chairman and the Faculty member in Charge of that Laboratory. It is the responsibility of researchers and laboratory supervisors to notify HSEO if any fume cupboards in their laboratory do not have an updated certification label.

If there is any question about the fume cupboard's operation, then OLS and HSEO should be called immediately. Whenever a new laboratory fume cupboard is installed, it is the responsibility of the laboratory supervisor to ensure that no hazardous substances are used in the fume cupboard until it is certified by HSEO. If any changes of any kind are made to the laboratory fume cupboard system, HSEO should be notified so that a new fume cupboard inspection can be conducted.

All laboratory fume cupboards in the department are equipped with a fume cupboard monitor which provides information on the status of the system. A green light indicates that the fume cupboard is functioning properly.

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

1. No fume cupboards should be used for work involving hazardous substances unless it has a certification label less than one year old.
2. Always keep hazardous chemicals at least six inches behind the plane of the sash.
3. Never put your head inside an operating laboratory fume cupboard to check an experiment. The plane of the sash is the barrier between contaminated and uncontaminated air.
4. Work with the fume cupboard sash in the lowest possible position. The sash will then act as a physical barrier in the event of an accident in the fume cupboard. Keep the sash closed when not conducting work in the fume cupboard. To save energy it is recommended to "turn off" a fume cupboard that is not currently used for hazardous operations or toxic chemical storage.

5. Do not clutter your fume cupboard with bottles or equipment. Keep it clean and clear. Only materials actively in use should be in the fume cupboard. This will provide optimal containment and reduce the risk of extraneous chemicals being involved in any fire or explosion which may occur in the fume cupboard.
6. Clean the grill along the bottom slot of the fume cupboard regularly so it does not become clogged with papers and dirt.
7. Promptly report any suspected fume cupboard malfunctions to OLS.
8. Be aware of the fume cupboard and Air-handler Maintenance Schedules (users receive notification from OLS by email). When a fume cupboard is under service, do not allow any toxic emissions to enter the fume cupboard. Both the chemical user and the person servicing the system may receive a harmful chemical exposure under such circumstances. Additionally, users will be notified of the air conditioner maintenance schedules. Shutting down the air conditioner impacts the performance of the air handlers, which may in some cases result in deterioration of the fume cupboard performance.

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

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

Prudent Practices in the Laboratory: Handling and Disposal of Chemicals, National Academy Press, 1995, pp. 178-193.

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

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

Copies of the *J. Chem. Ed.* articles are on file in the Chemistry Department Library of Lab Safety in Rm. 7127

4.5 Fire Extinguishers, Safety Showers, and Eyewash Facilities

Laboratory supervisors are required to instruct new personnel in the location and proper use of fire extinguishers, safety showers, and eyewashes *before* they begin research in the laboratory. HSEO offers a course in *Fire Extinguisher Training*, and the Department highly recommends that every experimentalist take this course to have a hands-on opportunity to put out a fire with a fire extinguisher. It is HKUST policy that personnel are not required to extinguish fires that occur in their work areas. However, as discussed in Chapter 5, under certain circumstances suitably trained personnel may attempt to extinguish fires. All laboratories in the Chemistry Department are provided with carbon dioxide extinguishers and generally several other types of extinguishers as well. All fire extinguishers should be mounted on a wall in an area free of clutter. Research personnel should be familiar with the location, use, and classification of the extinguishers in their laboratory. The types of extinguishers are described below, as well as their classification and suitability for use with different types of fires.

1. *Carbon dioxide extinguishers (BLACK)* 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 CO_2 extinguisher against fires involving alkali and certain other metals (such as Al, Mg, and Zn) and compounds such as lithium aluminium hydride.*

2. *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).

3. *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.

Water 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.

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 HSEO.

5.0 Standard Operating Procedures for Work with Hazardous Substances

5.1 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 the Chemistry Department laboratories. New and untested substances that may be hazardous are also frequently encountered. Thus, it is essential that all laboratory workers understand the types of toxicity, recognize the routes of exposure, and are familiar with the major classes of toxic and corrosive chemicals.

The most important single generalization regarding toxicity in chemical research is *treat all compounds as potentially harmful, especially new and unfamiliar materials, and work with them under conditions which will minimize exposure by skin contact and inhalation.*

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

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

5.1.1 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 Chapter 6. Select carcinogens (defined in detail in Chapter 6.1) 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 Chapter 5.2 below.

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

Table II. Listing of Carcinogenic Compounds by Reactivity or Functional Group. Select Carcinogens are marked with an asterisk.

- *Alkylating agents: α-halo ethers*
  - *bis(chloromethyl)ether
  - *methyl chloromethyl ether
- *Alkylating agents: sulfonates*
  - *1,4-butanediol dimethanesulfonate
  - diethyl sulfate
  - dimethyl sulfate
  - ethyl methanesulfonate
  - methyl methanesulfonate
  - methyl trifluoromethanesulfonate
  - 1,3-propanesultone
- *Alkylating agents: epoxides*
  - *ethylene oxide
  - diepoxybutane
  - epichlorohydrin
  - propylene oxide
  - styrene oxide
- *Alkylating agents: aziridines*
  - *ethylenimine
  - 2-methylaziridine
- *Alkylating agents: diazo, azo, and azoxy compounds*
  - 4-dimethylaminoazobenzene
- *Alkylating agents: electrophilic alkenes and alkynes*
  - *acrylonitrile
  - acrolein
  - ethyl acrylate
- *Acylating agents*
  - *β-propiolactone
  - δ-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 (iodomethane)
  - tetrachloroethylene
  - trichloroethylene
  - 2,4,6-trichlorophenol
- *Hydrazines*
  - *hydrazine (and hydrazine salts)
  - 1,2-diethylhydrazine
  - 1,1-dimethylhydrazine
  - 1,2-dimethylhydrazine
- N-*nitroso compounds*
  - **N*-nitrosodimethylamine
  - *N*-nitroso-*N*-alkylureas
- *Aromatic amines*
  - *4-aminobiphenyl
  - *benzidine (p,p'-diaminobiphenyl)
  - *α-naphthylamine
  - *β-naphthylamine
  - aniline
  - *o*-anisidine (2-methoxyaniline)
  - 2,4-diaminotoluene
  - *o*-toluidine (2-methylaniline)
- *Aromatic hydrocarbons*
  - *benzene
  - benz[a]anthracene
  - benzo[a]pyrene
- *Natural products (including antitumor drugs)*
  - adriamycin
  - aflatoxins
  - bleomycin
  - cisplatin
  - progesterone
  - reserpine
  - safrole
- *Miscellaneous organic compounds*
  - *formaldehyde (gas)
  - acetaldehyde
  - 1,4-dioxane
  - ethyl carbamate (urethane)
  - hexamethylphosphoramide
  - 2-nitropropane
  - styrene
  - thiourea
  - thioacetamide
- *Miscellaneous inorganic compounds*
  - *arsenic and certain arsenic compounds
  - *chromium and certain chromium compounds
  - *thorium dioxide
  - beryllium and certain beryllium compounds
  - cadmium and certain cadmium compounds
  - lead and certain lead compounds
  - nickel and certain nickel compounds
  - selenium sulfide

The preceding compounds were selected from lists of substances identified as carcinogens or potential carcinogens by OSHA, the International Agency for Research on Cancer (IARC), and the Annual Report on Carcinogens published by the National Toxicology Program (NTP). References in the Chemistry Department Safety Library (Rm. 7127) and the University Library should be consulted for additional information.

Note that those items listed above with an asterisk are "select carcinogens". They are therefore classified as "particularly hazardous substances" and are mentioned again in Chapter 6.

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*", whilst not themselves carcinogenic, can dramatically amplify the carcinogenicity of other compounds.

5.1.2 Reproductive and Developmental Toxins

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

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

Table III. Partial List of Reproductive Toxins

arsenic and certain arsenic compounds
benzene
cadmium and certain cadmium compounds
carbon disulfide
1,2-dibromo-3-chloropropane
1,2-dibromoethane
ethylene glycol monomethyl and ethyl ethers
ethylene oxide
lead compounds
mercury compounds
toluene
vinyl chloride
xylene

The above list is not intended to be complete, and it is the responsibility of the researcher and their laboratory supervisor to evaluate each compound involved in their work and to determine whether it should be handled as a reproductive toxin. Note that reproductive toxins are considered as "particularly hazardous materials" and is mentioned again in Chapter 6.

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 all skin contact with chemicals. Pregnant women and women intending to become pregnant should consult with their laboratory supervisor and the HSEO office with regard to the type of work they may safely perform and the special precautions they should take.

5.1.3 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).

5.1.4 Irritants

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

5.1.5 Toxic and Highly Toxic Agents

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

Table IV. OSHA Toxicity Definitions

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

It is important to note that the above classification does not take into consideration *chronic toxicity* (i.e. carcinogenicity and reproductive toxicity). Also, note that LD_{50} values vary significantly between different species, and the human toxicity for a substance may be greater or less than that measured in test terminals.

In evaluating the acute toxicity of chemical substances, the HMIS (Hazardous Materials Identification System) rating criteria developed by the National Paint and Coatings Association may be helpful. HMIS numbers can often be found in MSDS's. LD_{50} values can be found in MSDS's. This data is available on the "Sigma-Aldrich MSDS" CD-ROM over the HKUST network. This is available through the Windows 98 version of the Library Online System

i Choose "Library Online Systems"
ii Choose "Online Databases "
iii Choose "Complete List of Databases"
iv Choose "Science"
v Choose "Sigma-Aldrich MSDS"

You may then search for a particular MSDS by the chemical name, CAS Registry Number, formula, chemical family, name fragment. You may also search in references such as the Patnaik's *A Comprehensive Guide to the Hazardous Properties of Chemical Substances.*

Table V. HMIS Rating Criteria for Acute Toxicity

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

5.1.6 Hazardous Substances with Toxic Effects on Specific Organs

Substances included in this category include:

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

5.1.7 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.

5.1.8 Flammable and Explosive Substances

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

Table VI. Chemical Groups that Characterize Explosive Compounds

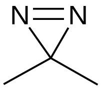
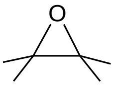
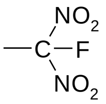
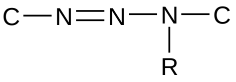
Bond Groupings	Class
-C≡C-	Acetylenic Compounds
-C≡C-metal	Metal Acetylides
-C≡C-X	Haloacetylene Derivatives
	Diazirines
RC=N=N:	Diazo compounds
RC-N=O	Nitroso compounds
RC-NO	Nitroalkanes, C–Nitro and Polynitroaryl compounds
RC(NO)	Polynitroalkyl compounds
R_3C-O-N=O	Acyl or alkyl nitrites
RC-ONO	Acyl or alkyl nitrites
	1,2-Epoxides
RC=N-O-Metal	Metal Fulminates or aci-Nitro Salts
 $-\overset{NO_2}{\underset{NO_2}{C}}-F$	Fluorodinitromethyl Compounds
RN-Metal	N-Metal Derivatives
RN-N=O	*N*-Nitroso Compounds
RN-NO	*N*-Nitro Compounds
RC-N=N-CR	Azo Compounds
RC-N=N-O-CR	Arenediazoates
RC-N=N-S-CR_3	Arenediazo Aryl Sulfides
RC-N=N-O-N=N-CR_3	Bis-Arenediazo Oxides
RC-N=N-S-N=N-CR_3	Bis-Arenediazo Sulfides
 $C-N=N-\underset{R}{N}-C$ (R = H, -CN, -OH, -NO)	Triazenes
-N=N-N=N-	High-Nitrogen Compounds; Tetrazoles
RC(O)OOR'	Peracids and Diacyl Peroxides
RCOOR'	Hydroperoxides and Dialkyl Peroxides
-O-O-Metal	Metal Peroxides, Peroxoacid Salts
-O-O-Non-metal	Peroxoacids
N-Cr-O	Amminechromium Peroxocomplexes
$-N_3$	Azides (Acyl, Halogen, Non-Metal, Metal, Organic)
$R_3C\text{-}N_2^+\ {}^-O\text{-}$	Arenediazoniumolates
$R_3C\text{-}N_2^+\ {}^-S\text{-}$	Diazonium Sulfides and Derivatives, "Xanthates"
$[R_3NH]^+\ Z^-$	Hydrazinium Salts, Oxosalts of Nitrogenous Bases
$[R_3N\text{-}OH]^+\ Z^-$	Hydroxylammonium Salts
$R_3C\text{-}N_2^+\ Z^-$	Diazonium Carboxylates or Salts
$[N\text{-}Metal]^+\ Z^-$	Aminemetal Oxosalts
Ar-Metal-X; X-Ar-Metal	Halo-Arylmetals
R_2N-X (R=N, X, C, H)	Halogen Azides - N-Halogen Compounds; N-Haloimides
$-NF_2$	Difluoroamino Compounds; N, N, N-trifluoroalkylamidines

Table VI. Chemical Groups that Characterize Explosive Compounds (cont.)

Bond Groupings	Class
-O-X	Alkyl Perchlorates; Chlorite Salts; Halogen Oxides; Hypohalites; Perchloric Acid and Perchlorates; Perchloryl Compounds

(The list of structures is taken in part from "Handbook of Reactive Chemical Hazards" L . Bretheric, 1985).

5.2 General Procedures for Work with Toxic Substances

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

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

1. **Preparation.**

   A cardinal rule of laboratory research is that workers must determine the potential hazards associated with an experiment *before* beginning it.

   Before working with any chemical, it is the responsibility of the researcher to determine what physical and health hazards are associated with the substance. This determination may require consulting library references and material safety data sheets, and may involve discussions with the laboratory supervisor and HSEO.

   Workers will be expected to show evidence of obtaining information as above or through presentation of printouts of MSDS data sheets or library references (see 3.2 above) when laboratory checks are carried out by the members of the Departmental Safety Committee or by HSEO.

2. **Minimize exposure to chemicals.**

   All skin contact with chemicals in the laboratory should be avoided. Use laboratory fume cupboards and other ventilation devices to prevent exposure to airborne substances whenever possible (note that the use of fume cupboards is **required** for work with lachrymators, stenches, experiments that evolve toxic gases, and for use of particularly hazardous substances; see Chapter 6).

3. **Do not underestimate risks.**

   Assume that any mixture of chemicals will be more toxic than its most toxic component. All new compounds and substances of unknown toxicity should be treated as toxic substances.

4. **Be prepared for accidents.**

   Before beginning an experiment, know what specific action you will take in the event of the accidental release of any hazardous substances involved (see Chapter 7.0, "Proper Planning of Laboratory Work"). Know the location of all safety equipment including fire extinguishers, fire blankets, eye washes, safety showers, spill carts and spill control materials, be familiar with the location of the nearest fire alarm and telephone, and know what telephone numbers to call in the event of an emergency. Know the location of the circuit breakers for your laboratory.

It should be evident from the discussion in Chapter 5.1 above that the majority of chemicals involved in research in Chemistry Department laboratories must be considered to be "hazardous substances". In addition to the four general principles outlined above, the following procedures should be standard practice for all work involving the use of hazardous substances.

5.2.1 Eye Protection

HKUST policy requires that all personnel, including visitors, wear eye protection *at all times* while in Chemistry Department laboratories. Not to do so is rated a serious offence, and disciplinary action may be incurred. Eye protection is discussed in detail in Chapter 4.1 of this Safety Manual.

5.2.2 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 Chapter 4.2. 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.

5.2.3 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 Table 1, Chapter 4.2 and *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.
e. Eating, drinking, smoking, gum-chewing, and applying cosmetics in laboratories is not permitted. Do not store food, beverages, cups, or other drinking and eating utensils in areas where hazardous chemicals are used or stored.

5.2.4 Avoid Inhalation of Toxic Substances

Inhalation of toxic vapors, mists, gases, or dusts can produce poisoning by absorption through the mucous membranes of the month, throat, and lungs, and can seriously damage these issues 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.

For this reason all 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 laboratory fume cupboard or other containment device. See Chapter 4.3 for a detailed discussion of laboratory fume cupboards.

If for lack of fume cupboard space researchers plan to routinely perform operations with volatile toxic substances outside the fume cupboard, HSEO must be consulted to monitor the airborne concentrations of the substances in question. The goal of such monitoring is to ensure that established exposure limits are not exceeded [such as Occupational Safety and health Administration (OSHA) Permissible Exposure Limits (PELs), American Conference of Governmental Industrial Hygienists Threshold Limit Values (TLVs) , or Hong Kong Labor Department OELs].

Never smell compounds of unknown toxicity.

5.2.5 Use and Maintenance of Equipment.

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

5.2.6 Use of Glassware

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

Careful handling and storage procedures should be used to avoid damaging glassware. Always carefully inspect glassware for flaws and cracks before use. Damaged items should be discarded or repaired.

Adequate hand protection should be used when inserting glass tubing into rubber stoppers or corks or when placing rubber tubing on glass hose connections. *An accident arising by fracture of glass in such an operation represents the most common source of injury in the laboratory*. The following is recommended:

a. The use of plastic or metal connectors should be considered for connecting plastic or rubber hosing to glass condensers; these are commercially available.
b. If connectors are not available, robust, protective linen gloves or gauntlets should be worn during any operation involving insertion of glass outlets/tubing/fixtures *etc* into stoppers or plastic/rubber tubing. A towel, or similar device used alone to protect the hands, is *not* recommended.
c. The plastic/rubber tubing may be fire-polished by the Departmental glassblower, or lubricated at the site of the operation by dipping the end in acetone, or better,

for operations conducted strictly within a fume hood, in chloroform, and applying it immediately to the glass outlet/tubing/fixture *etc*.

d. The glass must be held in a region immediately adjacent to the insertion point to minimize strain on the glass. If it turns out not to be possible to insert the glass tubing with *minimum* effort, the operation should not be attempted.

e. No attempt should be made to remove plastic/rubber tubing from a glass fixture by pulling it away. The excess plastic/rubber tubing beyond the glass fixture should be cut away. A sharp knife or scalpel should then be used to apply parallel cuts along the axis of the remaining plastic on each side to the end of the glass fixture. It should then be possible to peel away the plastic tubing with minimum effort. If the tubing is stuck to the glass, the glass fixture may be immersed in acetone to loosen the tubing.

The Department has purchased several glove types suitable for the foregoing operation. These are available from the DSO.

Glass-blowing operations should not be attempted. In a synthesis laboratory, these both constitute a fire hazard, and for inexperienced operators, represent a common cause of burns. The Department has a fully qualified glassblower.

Vacuum-jacketed glass apparatus should be handled with extreme care to prevent implosions. Equipment such as Dewar flasks should be taped or shielded. Only glassware designed for vacuum work should be used for that purpose.

Hand protection should be used when picking up broken glass. Small pieces should be swept up with a brush into a dustpan.

Broken glassware, syringes, and other "sharp objects" must be disposed of properly. Such waste should be separated from other trash and stored for pickup in clearly marked containers labelled "sharps".

5.2.7 Housekeeping

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

a. Work areas (including floors) should be cleaned regularly. Do not allow trash to accumulate.
b. Access to exits and safety equipment must not be obstructed.
c. All gas cylinders (tanks) should be secured to walls or benches.
d. Solvents should not be stored on the floor and large containers (more than 1 liter) must be stored below eye level (e.g. in cabinets).
e. Chemical storage refrigerators should be defrosted periodically and should not be overcrowded.
f. Fume cupboards must be cleaned regularly of paper and loose trash likely to block the uptake grill at the bottom of the hood.
g. Under no circumstance should fume hoods be used as a repository for dirty glassware, residual chemicals *etc.* The latter should be disposed of according to instructions in Chapter 12.

5.2.8 Work Conducted Outside Normal Hours

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

It is the responsibility of the researcher to design these experiments with provisions to prevent the release of hazardous substances in the event of interruptions in utility 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.

5.2.9 Children and Pets in Laboratories

Children are only permitted to visit the Department laboratories for brief periods of time and while under the *direct* supervision of their parent or other qualified adult. Even during a brief visit children must wear the appropriate personal protective equipment, such as Visitor Safety Glasses.

Pet animals such as dogs are not permitted in any laboratory in the Department of Chemistry.

5.2.10 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 should comply with Hong Kong FSD regulations (or OSHA regulations, in the absence of the relevant FSD regulation).

a. *To avoid the accumulation of excess chemicals, in so far as possible, always purchase the minimum quantities of commercial chemicals necessary for your research.*

   In the interest of accelerating research progress, maximizing consumable funding, and minimizing our storage requirements, it is advisable to check with other research groups before ordering a specialized chemical. If the item is already available in the department, under favorable circumstances you may find there is no need to order additional quantities.

b. All containers of chemicals should be properly labeled. *If a bottle is used to store a chemical for which it was not originally intended, the old label must be completely removed or obscured*, and the bottle should be clearly labelled with the correct contents so that there is no doubt whatsoever regarding what is contained.

c. All chemicals should be labelled with the date received. This is especially crucial for diethyl ether, tetrahydrofuran (THF) and other peroxidizables. Note that special HSEO guidelines apply for storage of diethyl ether and THF and these are given at the end of Chapter 5.3.2.

d. Only small quantities (less than 1 liter) of flammable liquids should be kept at work benches. Larger quantities should be stored in the yellow steel safety cabinets, or in the ventilated under-fume cupboard cabinets. Quantities greater than 1 liter should ideally be stored in metal or break-resistant containers.

e. Refrigerators used for storage of chemicals must be spark-proof, explosion-proof or laboratory-safe type units. Chemically resistant storage trays or secondary containers must be used to minimize the distribution of material in the event a container should leak or break.

f. Large containers (more than 1 liter) should be stored below eye-level on low shelves. Never store chemicals, hazardous or otherwise, on the floor.

g. Corrosive substances are ideally stored in the blue corrosive cabinets provided by OLS. If this is not possible, they should be stored in a chemically resistant cabinet.

h. Incompatible chemicals must be stored separately.
In particular:
- acids and bases must not be stored together.
- oxidizing and reducing agents must not be stored together. *Note that in this context nearly any organic can be considered a reducing agent--thus organic acids should not be stored with oxidizing mineral acids.*

i. Research groups should maintain an inventory list or card file of the hazardous substances present in their laboratories.

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

5.2.11 Transporting Hazardous Substances

HKUST policy requires that chemicals be transported between 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.

5.2.12 Disposal of Excess and Waste Chemicals

Detailed guidelines for the disposal of waste and excess chemicals are given in Chapter 12 "Hazardous Waste Management."

5.2.13 Procedures for Handling the Accidental Release of Hazardous Substances

If a minor spill occurs (in terms of quantity and/or hazard level), the user is responsible for clean up. For spills of extremely hazardous materials, or in the event of a large spill, the standard evacuation procedure (Chapter 13.1) should be followed.

Following successful neutralization and absorption of the spill, when HSEO judges the area is safe to enter, the USER is responsible to cleanup. The HSEO spill team may assist by providing the necessary equipment. EMO housekeeping staff ("cleaners") are not permitted to clean up spills of hazardous materials.

Experiments should always be designed so as to minimize the possibility of an accidental release of hazardous substances. Plan your experiments to use the minimal amounts of hazardous compounds practical and always transport such materials properly using break-resistant bottles or secondary containers. As discussed further below, develop a contingency plan to handle spills when working with hazardous substances.

In the event that a spill does occur, consult Chapter 13.1 and follow the Emergency Procedure given for a Hazardous Material Spill.

A. *Preplanning to Control Spills*

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

Every research group that works with hazardous substances should have a Spill Kit. Spill kits should be located near laboratory exits for ready access. Laboratory spill control kits should include:

i. *Inert absorbents* such as activated carbon for absorbing small spills of organic solvents.
ii. *Neutralizing agents for acid spills* such as sodium carbonate and sodium bicarbonate.
iii. *Neutralizing agents for alkali spills* such as sodium bisulfate.
iv. *Mercury spill kit*: note that in the event of a mercury spill great care should be exercised to recover all the spilled mercury. After cleanup HSEO should be contacted to measure the Hg vapor concentration, because the vapor pressure of mercury is 400 times higher than its threshold limit value (TLV). See Chapter 6.5, section (20) "Mercury."

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. Assisting persons should take care not to expose themselves to the chemical hazard. It is important to obtain medical attention as soon as possible; call 8999, the Security Office 24 hour line in the event of an emergency.

For spills covering small amounts of skin, immediately flush with flowing water for no less than fifteen minutes. If there is no visible burn, wash with warm water and soap, 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. Speed is essential, and no time should be wasted because of modesty. Be careful not to spread the chemical on the skin, or especially in the eyes. Use caution when removing pullover shirts or sweaters to prevent contamination of the eye; it may be better to cut the garments off. Immediately flood the affected body area with warm water for at least 15 minutes. Resume if pain returns. Do not use creams, lotions or salves. Get medical attention as soon as possible. Contaminated clothes should be discarded or laundered separately from other clothing.

For splashes into the eye, immediately flush the eye with potable water from the emergency eye wash using a gently flowing stream for at least 15 minutes. Hold the eyelids away from the eyeball, move the eye up and down and sideways to wash thoroughly behind the eyelids. The eyewash should be used, but if this is inaccessible to the injured person, he/she should be placed on their back and water gently poured into their eyes for at least fifteen minutes. First aid must be followed by prompt treatment by a member of a medical staff or an ophthalmologist especially acquainted with chemical injuries.

C. *Notify Personnel in the Area*

Alert other workers in the laboratory of the accident and the nature of the chemicals involved. In the event of the release of a highly toxic gas or volatile material, the laboratory must be evacuated. In so doing, the emergency ventilation button adjacent to the exit door leading to the outside corridor must be pressed in order to activate the emergency ventilation, and to activate the emergency yellow warning light outside the laboratory.

Under no circumstance should any Departmental personnel attempt to reenter a laboratory once the yellow light is flashing. The pressing of the emergency ventilation button will also activate an alarm in the Security Office who will respond by contacting HSEO, and by initiating their own measures to prevent ingress into the affected laboratory. In any event, the Security Office (ext. 8999) should be contacted immediately to ensure that a response is forthcoming. The Security Office will also make use of the Public Address System to notify laboratory users of the location of the spill and advise appropriate evacuation routes. See Chapter 13.0 for a discussion of two important notification principles: "multiple parallel notification" and "full disclosure."

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 fume cupboard), 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.

Don't clean anything up unless you know what it is and what hazard it presents.

i *Materials of low flammability which are not volatile or which have low toxicity.* This category of hazardous substances includes inorganic acids (sulfuric, nitric) and caustic bases (sodium and potassium hydroxide). For clean-up, wear appropriate protective apparel including gloves and (if necessary) shoe-coverings. Neutralize the spilled chemicals with materials such as sodium 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 this section.

ii *Flammable solvents.* Fast action is crucial in the event that a flammable solvent of relatively low toxicity is spilled. This category includes petroleum ether, hexane, pentane, diethyl ether, dimethoxyethane, and tetrahydrofuran. Immediately alert other workers in the laboratory, extinguish all flames, and turn off any spark-producing equipment. In some cases the power to the lab should be shut off with the emergency circuit-breaker. As quickly as possible, the spilled solvent should be soaked up using the activated carbon absorbent. These should be sealed in labelled containers and disposed of properly.

iii *Highly toxic substances.* Do not attempt to clean up a spill of a highly toxic substance by yourself. Notify other personnel of the spill and contact the HSEO to obtain assistance in evaluating the hazards involved. The Security Office and Fire Services have special protective equipment to permit safe entry into areas contaminated with highly toxic substances.

E. ***Handling Leaking Gas Cylinders*** (See also Chapter 14.3.4)

If you are to handle gas cylinders, even on an occasional basis, you should take the HSEO course *'Safety with 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, prompt action must be taken:

i. If the cylinder is small it should be moved to a fume cupboard, and HSEO should be called immediately to assist in the disposal or repair of the leaking cylinder.
ii. If the cylinder cannot be moved, and the gas is toxic, corrosive or flammable, activate the emergency ventilation button, and evacuate the area.

5.3 General Procedures for Work with Flammable and Explosive Substances

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

Table VII. Flash Points of Common Solvents

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

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 Table VII, many common laboratory solvents and chemicals have flash points that are lower than room temperature and are potentially very dangerous.

5.3.1 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 (such as 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. Great caution should be used when using hot plates as a heat source for recrystallization. The recrystallization should be performed in a Fume Cupboard with the sash up to maximize air flow. Never leave such an operation unattended, as boil-over and buildup of flammable vapors have been known to lead to fire.
4. When transferring flammable liquids in metal equipment, static-generated sparks should be avoided by bonding and the use of ground straps.
5. Ventilation is one of the most effective ways to prevent the formation of flammable mixtures. A laboratory Fume Cupboard should be used whenever appreciable quantities of flammable substances are transferred from one container to another, allowed to stand or heated in open containers, or handled in any other way. Be sure that the fume Cupboard is free of all ignition sources.

5.3.2 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. See Table VI in Chapter 5.1.8 for a listing of explosive functional groups and Appendix V for explosive substances. Special precautions are required for the safe use of explosive materials. *It is the responsibility of the researcher to evaluate the explosive hazards involved in their work and to consult with their supervisor to develop detailed standard operating procedures for any work involving explosive substances.* Work with explosive materials will generally require the use of special protective apparel (face shields, gloves, lab coats) and protective devices such as explosion shields and barriers.

Organic peroxides are among the most hazardous substances handled in Chemistry Department laboratories. As a class, they are low-power explosives, hazardous because of their sensitivity to shock, sparks, and even friction (such as is generated when a cap is 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 (MCPBA), benzoyl peroxide, hydrogen peroxide, and *t* -butyl hydroperoxide. Pure MCPBA is dangerous; most companies supply technical grade material which is 50-70% MCPBA, the remainder being *m*-chlorobenzoic acid. Extreme caution should be used when employing MCPBA of higher than 70% purity. Likewise, extreme caution should be used when employing hydrogen peroxide solutions of 30% or greater purity. In particular, contact with metals (such as a syringe needle) should be avoided. Heating reactions that contain MCPBA, hydrogen peroxide, or *t*-butyl hydroperoxide is never recommended

The greatest peroxide risk faced by most chemists is posed by common solvents and reagents which form peroxides (hydroperoxides) on exposure to air. Classes of compounds that form peroxides by autoxidation are included in Table VIII:

Table VIII. Peroxidizable Functional Groups (listed in approximate decreasing order of hazard)

a. **Certain Alkali Metals, Alkali Metal Amides, Metal Alkoxides, and Metal Alkyls**
Some of these materials are extremely hazardous and autoxidize nearly instantly upon contact with air. Examples include potassium, rubidium, cesium, sodium amide, and potassium amide. Extreme caution is advised when using the later two reagents. In general it is almost always preferable to generate these materials as needed by dissolving the required amount of metal in liquid ammonia in the presence of a Fe(III) catalyst.

b. **Ethers and Acetals with α-Hydrogen Atoms**
Examples include diethyl ether, THF, dioxane, 1,2-dimethoxyethane (DME), ethyl vinyl ether and alcohols protected as THP ethers. Diisopropyl ether is especially prone to autoxidation and even small quantities of it should not be heated, concentrated, or distilled without passing through an alumina column immediately beforehand. HSEO has established guidelines for the storage and labeling of diethyl ether and THF; these are given at the end of this section.

c. **Vinyl halides, esters and ethers, chloro- and fluoroolefins**

d. **Conjugated dienes, enynes, and diynes,** among which divinylacetylene is particularly hazardous.

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

f. **Saturated hydrocarbons with exposed tertiary hydrogens;** common peroxide-formers include decalin (decahydronaphthalene) and 2,5dimethylhexane.

g. **Aldehydes, and Ketones that possess an α-Hydrogen.**

h. **Secondary Alcohols.**

i. **Ureas, Amides, and Lactams that possess an α-hydrogen on the carbon atom attached to nitrogen.**

(List based on *Prudent Practices for Disposal of Chemicals from Laboratories*, Appendix I)

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 containing crystallized material; contact HSEO 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 KI solution, and shake. The appearance of a yellow to brown color indicates the presence of peroxides. (Note that freshly prepared KI solution must be used, as this reagent oxidizes on standing to a yellow solution).

or

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

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

HSEO Guidelines for Storage of Diethyl Ether

To mitigate the risk of peroxide buildup in solvent bottles, HSEO formulated the following guidelines for the storage and labeling of diethyl ether.

1. Bottles must be dated when received and should be affixed with the label designed by HSEO, which incorporates a space for "retest date".

2. Opened bottles should be tested for peroxides after one month and at one month intervals until the contents are consumed.

3. Unopened bottles should be disposed of or tested for peroxides after one year.

The Chemistry Safety Committee recommends that this practice also be carried out for THF, since this solvent is widely used in the department.

To minimize the testing and retesting that needs to be done, the following practice is recommended:

a. Minimize the number of bottles of diethyl ether or THF that are open at any given time (try to open and use only one bottle at a time!). If open bottles are used up within 30 days, then there will never be any need to test them.

b. Order these solvents when you need them, in a quantity such that they would be consumed in 3 months or less.

5.3.3 Control of Fires

HKUST does not require faculty, staff, or students to fight fires.

The complete emergency response procedure for dealing with laboratory fires is given in Chapter 13.3 and all researchers should be thoroughly familiar with it.

Two additional guidelines are given below to assist personnel in deciding whether or not to fight a fire:

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

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

5.3.4 Specific Hazards That May Lead to Fires or Explosions

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

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

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. *Azides* such as sodium azide can displace halide from chlorinated hydrocarbons such as dichloromethane to form highly explosive organic polyazides; this substitution reaction is facilitated by the presence of solvents such as DMSO.

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

6. *Carbon disulfide* is both very toxic and very flammable; mixed with air, its vapors can be ignited by a steam bath or pipe, a hot plate, or by a glowing light bulb.

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

8. *Diazomethane* and related compounds should be treated with extreme caution. They are very toxic (potent carcinogens), and the pure gases and liquids explode readily. Solutions in ether are safer with regard to shock sensitivity.

9. *Dimethyl sulfoxide* decomposes violently on contact with a wide variety of active halogen compounds. Explosions from contact with active metal hydrides have been reported.

10. *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 (see 5.3.2 above).

11. *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.

12. *Halogenated compounds* such as chloroform, carbon tetrachloride, and other halogenated solvents should be dried with sodium, potassium, or other active metals; violent explosions usually occur upon treatment of these solvents with active metals.

13. *Hydrogen peroxide* stronger than 3% can be dangerous: in contact with the skin, it may cause severe burns. 30% hydrogen peroxide can decompose violently if contaminated with iron, copper, chromium, or other metals or their salts.

14. *Liquid-nitrogen cooled traps* open to the atmosphere rapidly condense liquid air. The liquid oxygen component of liquid air may immediately cause an explosion if it comes in contact with an organic substance in the trap. More commonly however an explosive pressure buildup often occurs upon removal of the coolant. Such an explosion usually occurs with enough force to shatter glass equipment. Hence, only sealed or evacuated equipment should be cooled with liquid nitrogen.

15. *Lithium aluminium hydride (LAH)* should not be used to dry ethyl ether or tetrahydrofuran; fires from this are very common. The products of the reaction of LAH with carbon dioxide have been reported to be explosive. Carbon dioxide or bicarbonate extinguishers should not be used against lithium aluminum hydride fires, which should be smothered with sand or some other inert substance.

16. *Oxygen tanks*: Serious explosions have resulted from contact between oil and high-pressure oxygen. Oil should not be used on connections to an oxygen cylinder. Regulators used for compressed air or industrial grade nitrogen can never be substituted for an oxygen regulator, since they often suffer pump oil contamination.

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

18. *Palladium or platinum on carbon, platinum oxide, Raney nickel, and other catalysts* should be filtered from catalytic hydrogenation reaction mixtures carefully. The recovered catalyst is usually saturated with hydrogen and is

highly reactive and thus will enflame spontaneously on exposure to air. When filtering hydrogenation reaction mixtures (particularly large-scale reactions), the filter cake should not be allowed to become dry. The funnel containing the still-moist catalyst filter cake should be put into a water bath immediately after completion of the filtration. Note that another hazard in working with such catalysts is the danger of explosion if additional catalyst is added to a flask in which hydrogen is present.

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

20. *Perchlorates* should be avoided whenever possible. Perchlorates should not be used as drying agents if there is a possibility of contact with organic compounds, or if they will be in proximity to a dehydrating acid strong enough to concentrate the perchloric acid to more than 70% strength (e.g., in a drying train that has a bubble counter containing sulfuric acid). Safer drying agents should be used. Any experiments involving heated perchloric acid or perchloric acid evaporations should be carried out in a specially designed "Perchloric Acid Fume Cupboard". At the present time none of these type of fume cupboards are installed in the Chemistry Department, but a few are installed at other locations at HKUST. HSEO should be contacted well in advance to arrange access to one of them. Seventy percent perchloric acid can be boiled safely at approximately 200 °C, but contact of the boiling undiluted acid or the hot vapor with organic matter, or even easily oxidized inorganic matter (such as compounds of trivalent antimony), will lead to serious explosions. Oxidizable substances must never be allowed to contact perchloric acid. Beaker tongs, rather than rubber gloves, should be used when handling fuming perchloric acid. Perchloric acid evaporations should be carried out in a Perchloric Acid Fume Cupboard that has a good draft and a built-in water spray for the ductwork behind the baffle. Frequent (weekly) washing out of the fume cupboard and ventilator ducts with water is necessary to avoid danger of spontaneous combustion or explosion if this acid is in common use.

21. *Permanganates* are explosive when treated with sulfuric acid. When both compounds are used in an absorption train, an empty trap should be placed between them.

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

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

24. *Phosphorus trichloride* reacts with water to form phosphorous acid which decomposes on heating to form phosphine, which may ignite spontaneously or explode. Care should be taken in opening containers of phosphorous trichloride, and samples that have been exposed to moisture should not be heated without adequate shielding to protect the operator.

25. *Potassium* is in general more reactive than sodium; it ignites quickly on exposure to humid air and, therefore, should be handled under the surface of a

hydrocarbon solvent such as mineral oil or toluene. Oxidized coatings should be carefully scraped away before cutting potassium metal as explosions can otherwise occur.

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

27. *Sodium* should be stored in a closed container under kerosene, toluene, or mineral oil. Procedures for destruction of sodium are given in Section 12.2.2 below. Contact with water should be avoided because sodium 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.

[The above list is based on *Prudent Practices for Handling Hazardous Chemicals in Laboratories* (1981) p. 68-72.]

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

Table IX. Examples of Incompatible Chemicals

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

Cyanides	Acids
Decaborane	Carbon tetrachloride and some other halogenated hydrocarbons

Table IX. Examples of Incompatible Chemicals (cont.)

Chemical	**Is Incompatible With**
Flammable liquids	Ammonium nitrate, chromic acid, hydrogen peroxide, nitric acid, sodium peroxide, halogens
Fluorine	Everything
Hydrocarbons	Fluorine, chlorine, bromine, chromic acid, sodium peroxide
Hydrocyanic acid	Nitric acid, alkali
Hydrofluoric acid (anhydrous)	Ammonia (aqueous or anhydrous)
Hydrogen peroxide	Copper, chromium, iron, most metals or their salts, alcohols, acetone, organic materials, aniline, nitromethane, combustible materials
Hydrogen sulfide	Fuming nitric acid, oxidizing gases
Hypochlorites	Acids, activated carbon
Iodine	Acetylene, ammonia (aqueous or anhydrous), hydrogen
Mercury	Acetylene, fulminic acid, ammonia
Nitrates	Sulfuric Acid
Nitric Acid (concentrated)	Acetic acid, aniline, chromic acid, hydrocyanic acid, hydrogen sulfide, flammable liquids, flammable gases, copper, brass, any heavy metals
Nitrites	Acids
Nitroparaffins	Inorganic bases, amines
Oxalic Acid	Silver, Mercury
Oxygen	Oils, grease, hydrogen, flammable liquids, solids, or greases
Perchloric Acid	Acetic anhydride, bismuth and its alloys, alcohol, paper, wood, grease, oils
Peroxides, organic	Acids (organic or mineral), avoid friction, store cold
Phosphorous (white)	Air, oxygen, alkalis, reducing agents
Potassium	Carbon tetrachloride, carbon dioxide, water
Potassium Chlorate	Sulfuric and other acids
Potassium perchlorate (see also Chlorates)	Sulfuric and other acids
Potassium permanganate	Glycerol, ethylene glycol, benzaldehyde, sulfuric acid
Selenides	Reducing agents
Silver	Acetylene, oxalic acid, tartaric acid, ammonium compounds, fulminic acid
Sodium	Carbon tetrachloride, carbon dioxide, water
Sodium 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

6.0 Procedures for Work with Particularly Hazardous Substances

6.1 Identification and Classification of Particularly Hazardous Substances

As discussed in the previous section (Chapter 5) of this Safety Manual, 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 Chapter 5.

There are some substances, however, that pose such significant threats to human health that they are classified as "particularly hazardous substances" (PHS's). The OSHA Laboratory Standard requires that special provisions be established to prevent the harmful exposure of researchers to PHS's. General procedures for working with such materials are presented in detail in Chapters 6.3 and 6.4 below.

A chemical is classified as a *particularly hazardous substance* if it falls into one or more of the following three hazard categories:

1. select carcinogen
2. reproductive and/or developmental toxin
3. highly acutely toxic substance

Compounds so classified generally must then be handled using the procedures outlined in Chapter 6.3 below. Note, however, that in some circumstances (e.g. when very small quantities of material are being used) it may not be necessary to employ all of the special precautions described in Chapter 6.3. It is the responsibility of the laboratory supervisor to determine whether a compound is to be treated as a "particularly hazardous substance" in the context of its specific use in his or her laboratory. Note that materials belonging to either of the first two categories are considered to possess high chronic toxicity; additional precautions apply for the use of such materials

6.1.1 Select Carcinogens

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

a. It is regulated by OSHA as a carcinogen,

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

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

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

i after inhalation exposure of 6-7 hours per day, 5 days per week, for a significant portion of a lifetime to dosages of less than 10 mg/m^3

ii after repeated skin application of less than 300 mg/kg of body weight per week; or

iii after oral dosages of less than 50 mg/kg of body weight per day.

The following Table lists the substances meeting criteria a., b., or c..

Table X. Partial List of Select Carcinogens in Alphabetical Order

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

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

6.1.2. Reproductive and Developmental Toxins

A partial list of Reproductive and Developmental Toxins is given as Table III in Chapter 5.1.2.

Reproductive toxins act during pregnancy and cause adverse effects on the fetus; these effects include embryolethality (death of fertilized egg, embryo or fetus), malformations (teratogenic effects), and postnatal functional defects. Examples of embryotoxins include thalidomide and certain antibiotics such as tetracycline. Women of childbearing potential should note that embryotoxins have the greatest impact during the first trimester of pregnancy. *Because a woman often does not know that she is pregnant during this period of high susceptibility, special caution is advised when working with all chemicals, especially those rapidly absorbed through the skin (e.g., formamide).* Pregnant women and women intending to become pregnant should consult with their laboratory supervisor and HSEO before working with substances that are suspected to be reproductive toxins. As minimal precautions, the general procedures outlined in Chapter 6.3 below should then be followed for work with such compounds.

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

6.1.3. Compounds with a High Degree of Acute Toxicity

Compounds that have a high degree of acute toxicity comprise a third category of particularly hazardous substances as defined by the OSHA Lab Standard. Acutely toxic agents include certain corrosive compounds, irritants, sensitizers (allergens), hepatotoxins, nephrotoxins, neurotoxins, agents that act on the hematopoietic systems, and agents which damage the lungs, skins, eyes, or mucous membranes (see Chapter 5.1 for definitions of these classes of hazardous substances). Substances which have a high degree of acute toxicity are interpreted by OSHA as being substances which "may be fatal or cause damage to target organs as the result of a single exposure or exposures of short duration". "Toxic" and "highly toxic" agents are defined by OSHA regulations (29 CFR 1910.1200 Appendix IV) which are summarized in Table IV in Chapter 5.1.5. The following Table lists some of the compounds that may be in current use in Chemistry Department laboratories and which have a high degree of acute toxicity:

Table XI. Partial List of Compounds with a High Degree of Acute Toxicity

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

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

Compounds classified as having a high degree of acute toxicity must generally be handled using the procedures outlined in Chapter 6.3 below. Note, however, that in some circumstances (e.g. when very small quantities of material are being used) it may not be necessary to employ all of the special precautions described in Chapter 6.3. 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.

Several of the compounds listed above require prior approval from the Department Safety Committee before work with them can be carried out. See Chapter 8 for a discussion of prior approval requirements.

In evaluating the hazards associated with work with toxic substances, it is important to note that a number of factors influence the response of individuals to exposure to toxic compound. For example, people are rarely exposed to a single biologically active substance. Note that one toxin can influence the effect of a second. Examples are the dramatically enhanced lung carcinogenicity of combined exposure to asbestos and tobacco smoke, and the potentiating activity of phorbol esters on skin carcinogenesis initiated by polycyclic hydrocarbons. There are insufficient data at present to identify which substances potentiate (or possibly even antagonize) the effects of others, but it is important for laboratory workers to be aware that such interactions can occur.

The response of an organism to a toxin typically increases with the dose given, but the relationship is not always linear. As one example, some carcinogenic alkylating agents show a biphasic dose-mutation curve featuring a "break-point" at which the slope increases dramatically going left to right (somewhat resembling a "hockey stick"). 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.

Thus a cautious approach must be taken in handling all chemicals in the workplace.

The foregoing underscores the importance of maintaining good laboratory practices at all times, and with all chemicals.

6.2 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 fume cupboard which is posted with warning signs that ensure that all employees working in the area are informed of the hazardous substances in use there.

It is the responsibility of laboratory supervisors to define the designated areas in their laboratories and to post these areas with conspicuous signs reading "DESIGNATED AREA FOR USE OF PARTICULARLY HAZARDOUS SUBSTANCES--AUTHORIZED PERSONNEL ONLY". Printed signs can be obtained from the Chairman of the Department Safety Committee. 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 fume cupboards serve as designated areas for most of the research groups in the Chemistry Department. Laboratory supervisors are required to notify the Department Chemical Safety Committee Chairman and HSEO of the specific location of any designated areas established in their research groups *which are not laboratory fume cupboards.*

6.3 General Procedures for Work with Substances of Moderate to High Chronic Toxicity or High Acute Toxicity

The following general procedures should be followed in work with substances with *high acute toxicity* - i.e. substances that can be fatal or cause serious damage to target organs as the result of a single exposure of short duration. These procedures should also be employed in laboratory operations using those *carcinogens* and *reproductive toxins* for which infrequent, small quantities do not constitute a significant hazard, but which can be dangerous to workers exposed to high concentrations or repeated small doses. A substance that is not known to cause cancer in humans, but which has shown statistically significant, but low, carcinogenic potency in animals, generally should also be handled according to the procedures outlined in this section. Work with more potent carcinogens and reproductive toxins requires the additional precautions described in Chapter 6.4 below. Keep in mind that all of the general rules for work with toxic substances discussed in Chapter 6.5 of this Safety Manual also apply to work with "particularly hazardous substances".

1. Information

Before beginning a laboratory operation, each researcher must consult the appropriate literature (see 3.2) 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 Chapter 6.4.

2. Zero skin contact

Contact with the skin is a frequent mode of chemical injury. Many toxic substances are absorbed through the skin with sufficient rapidity to produce systemic poisoning. *Avoid all skin contact with particularly hazardous substances* by using suitable protective apparel including the appropriate type of gloves (see *Prudent Practices*, pp. 158-160) or gauntlets (long gloves) and a suitable laboratory coat or apron which covers all exposed skin. See Chapter 4.2 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 fume cupboards

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 Fume Cupboard or other suitable containment device.* The Fume Cupboard should have been previously certified by HSEO. See Chapter 4.3 for further discussion of the operation of laboratory fume cupboards.

4. Be prepared for accidents

The laboratory worker should always be prepared for possible accidents or spills involving toxic substances. See Chapter 7, "Proper Planning of Laboratory Work." To minimize hazards from accidental breakage of apparatus or spills of toxic substances in the fume cupboard, 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 fume cupboard can be fitted with a removable liner of adsorbent plastic-backed paper. Such procedures will contain spilled toxic substances in a pan, tray, or adsorbent liner and greatly simplify subsequent cleanup and disposal.

If a major release of a particularly hazardous substance occurs outside the fume cupboard, then the emergency ventilation button must be actuated, and the room or appropriate area should be evacuated and necessary measures taken to prevent exposure of other workers (see 5.2.12). HSEO should be contacted for assistance and equipment for spill clean-up; personnel can be contacted for assistance after working hours by calling Security Office (ext. 8999). 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 fume cupboard, a supplied-air full-face respirator should be worn (only persons approved by HSEO can wear such apparatus). Contaminated clothing and shoes should be thoroughly decontaminated or incinerated. See Chapter 5.2 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 fume cupboard exhaust air. The general waste disposal procedures outlined in Chapter 5.2 should be followed.

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 fume cupboard. If practical, *waste materials and waste solvents containing toxic substances should be decontaminated chemically by some procedure that can reasonably be expected to convert essentially all of the toxic substances to nontoxic substances* (for a discussion, see *Prudent Practices for Disposal of Chemicals from Laboratories* , pp. 56-100 and *Destruction of Hazardous Chemicals in the Laboratory* by G. Lunn and E. B. Sansone).

If chemical decontamination is not feasible, the waste materials and solvents containing toxic substances should be stored in closed, impervious containers so that personnel handling the containers will not be exposed to their contents. In general, liquid residues should be contained in glass or polyethylene bottles. All containers of toxic wastes should be suitably labeled to indicate the contents (chemicals and approximate amounts) and the type of toxicity hazard that contact may pose. For example, containers of wastes from experiments involving appreciable amounts of weak or moderate carcinogens should carry the warning: CANCER SUSPECT AGENT. All wastes and residues that have not been chemically decontaminated in the exhaust fume cupboard where the experiment was carried out should be disposed of in a safe manner that ensures that personnel are not exposed to the material (see Chapter 12, Hazardous Waste Management).

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. In addition, it may be advisable to keep records of the amounts of material used and names of workers involved.

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

   Those operations involving particularly hazardous substances in which there is the possibility of the accidental release of harmful quantities of the toxic substance must be carried out in designated areas. As discussed in Chapter 6.2, in the Chemistry Department many laboratory fume cupboards 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.

6.4. Additional Procedures for Work with Substances of Known High Chronic Toxicity

Substances of "Known High Chronic Toxicity" include *Select Carcinogens* (Chapter 6.1.1) and *Reproductive and Developmental Toxins* (Chapter 6.1.2) as well as certain heavy metal compounds such as dimethylmercury and nickel carbonyl.

In addition to the procedures and precautions described in the preceding section, 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), additional precautions must be taken. 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.

1. **Approvals**

   Permission must be obtained from your research supervisor prior to any work with substances of known high chronic toxicity.

   It is the supervisor's responsibility to approve all plans for experimental operations and waste disposal. In addition, note that prior approval from the Chemistry Department Safety Committee is required for work with certain extremely hazardous substances (see Chapter 8).

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 Chapter 6.2), 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 cupboards).

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

3. Wear suitable protective apparel

Proper gloves should be worn when transferring or otherwise handling substances or solutions of substances having high chronic toxicity (see *Prudent Practices* , pp. 158-160). Two gloves should generally be worn on each hand. In the event of an accident, the outer, 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. Non-disposable protective apparel should be thoroughly washed (in such a way that does not expose the "washer"). Note that the fluid used to wash will be contaminated and must be disposed of properly.

4. Protect the environment and dispose of waste materials properly

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

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

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

5. Be prepared for accidents

Be prepared for the release of a substance of high chronic toxicity by formulating a contingency plan to deal with any accident which may occur. HSEO can provide assistance in preparing these contingency plans. Make sure that the necessary equipment and materials are on hand to deal with possible accidents before beginning work with substances of high chronic toxicity.

6. Medical Surveillance

If you anticipate being involved in continued experimentation with a substance of high chronic toxicity (i.e., if you regularly use toxicologically significant quantities of such a substance three times a week), then a qualified physician should be consulted to determine whether it is advisable to establish a regular schedule of medical surveillance or biological monitoring. See Chapter 10 for a further discussion of medical surveillance.

6.5 Specific 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 Chemistry Department laboratories. The information presented in this section is not meant to be complete.

Researchers should consult the appropriate literature (see Chapter 3.2) and their laboratory supervisor before working with these particularly hazardous substances.

6.5.1 Acrylonitrile

Acrylonitrile is regulated as a probable human carcinogen by OSHA and also is listed as a substance with a moderate degree of acute toxicity (oral LD_{50} (rat) is 78 mg/kg). The PEL (permissible exposure limit) is 2 ppm; the TLV-TWA (threshold limit value - time-weighted average) is also 2 ppm. Acrylonitrile is severely irritating to the eyes and mildly irritating to the skin; prolonged contact with the skin can lead to burns. Acrylonitrile is a highly flammable liquid; its vapor forms explosive mixtures with air. *Work involving significant quantities of acrylonitrile should be conducted using the general procedures outlined in both Chapters 6.3 and 6.4.* In particular, work with acrylonitrile should be conducted in a fume cupboard to prevent exposure by inhalation; splash goggles and impermeable gloves should be worn at all times to prevent eye and skin contact.

6.5.2 Benzene

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

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

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

Benzene should normally not be used as a solvent in the Department of Chemistry. Based on consultation with supervisor, it may be possible to use toluene if no other solvent is suitable for the task at hand.

If benzene is to be used in significant quantities, approval of the supervisor must first be obtained. The operation must then be conducted employing the general procedures outlined in Chapter 6.3; all operations in which there is the possibility of the accidental release of benzene at or above the PEL should be carried out in a designated area.

6.5.3 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 irritant to the eyes of rats. Rats and hamsters subjected to 10 or 30 6-hour exposures of 1 ppm BCME showed evidence of tracheal and bronchial hyperplasia, as well as effects on the central nervous system. BCME is carcinogenic to mice following inhalation, skin application, or subcutaneous administration. In newborn mice, it is carcinogenic by inhalation and subcutaneous administration. BCME is a lung carcinogen in humans.

The TLV (threshold limit value) for BCME is 0.001 ppm (1 ppb; 5 mg/m^3). The substance is classified by ACGIH as a human carcinogen. OSHA has classified BCME as a cancer-suspect agent and has stringent regulations (29 CFR 1910.1008) for its use if its concentration in a material exceeds 0.1%. *Work involving chloromethyl ether derivatives must be carried out using the general procedures outlined in Chapters 6.3 and 6.4. Prospective users of chloromethylether derivatives should note the caution for bis(chloromethyl) ether given in Organic Syntheses Collective Volume V, p. 218.*

Researchers planning to carry out a chloromethylation reaction by using formaldehyde and HCl should note that bis(chloromethyl) ether and its derivatives are generated by this procedure. If the bromomethyl derivative can be used in place of the chloromethyl derivative, synthesis of the former is highly recommended, since it is reported that bromomethylation can be performed without generating any positive Ames Test species (van der Made, *J. Org. Chem.* **1993**, *58*, 1262).

6.5.4 Bromine

Fourteen mg/kg of bromine is a lethal oral dose for humans; exposure to 10 ppm is immediately dangerous to life and health (IDLH). Inhalation of bromine has caused coughing, nosebleeds, dizziness, and headache, followed after some hours by abdominal pain, diarrhea, and skin rashes. Severe irritation of the respiratory passages and pulmonary edema can also occur. Lacrimation occurs at levels of less than 1 ppm. It is reported that 40-60 ppm are dangerous for short exposures, and 1000 ppm can be fatal. The substance produces irritation and destruction of the skin with blister formation. Severely painful and destructive eye burns may result from contact with either liquid or concentrated vapors of bromine.

Bromine is moderately toxic to animals via the inhalation route and slightly toxic via the oral route: LC_{50} (mice, 1.7-hour inhalation) = 240 ppm; LD_{50} (rats, oral) = 3100 mg/kg. The respiratory irritation threshold for bromine in rats is 1.4 ppm.

Rats fed 0.01 mg/kg bromine for 6 months experienced changes in their conditional reflexes and several blood indexes. Rats, mice, and rabbits inhaling 0.2 ppm of bromine for 4 months developed disturbances in the functions of their respiratory, nervous, and endocrine systems; 0.02 ppm did not cause any adverse effects.

The TLV and the OSHA PEL for bromine are 0.1 ppm (0.7 mg/m^3) as an 8-hour time-weighted average. The exposure limit suggested by ACGIH is 0.3 ppm over any 15-min period.

Splash goggles and rubber gloves (double gloves!) should be worn when handling more than a few milliliters of pure liquid bromine. Although the irritating odor of bromine provides a warning, all operations with it must be carried out in a hood. Accidental contact with the skin must be immediately counteracted by washing with water.

A worker whose clothing has been doused with liquid bromine is in severe danger unless the affected clothing is removed immediately.

6.5.5 Carbon Disulfide

Carbon disulfide is rapidly absorbed when inhaled, and inhalation can produce acute poisoning. Poisoning can also occur from ingestion; death has been known to occur after ingestion of as little as 15 ml.

Acute poisoning by ingestion or inhalation can produce narcosis, accompanied by delirium. This may progress to areflexia, paralysis, coma, and death. Mental disorders or polyneuritis have been reported as sequelae. It is reported that exposure in excess of 500 ppm is required before acute effects will be noted.

Poisoning resulting from chronic exposure was reported frequently in the older literature but rarely in the last 10 to 20 years. Chronic exposure has resulted in neuropsychiatric manifestations with mental disorders, including psychoses, weakness, paralysis, parkinsonism, and blindness or in polyneuritis with pain along nerves, loss of strength, and paresthesias.

In milder exposures, the reported effects have been attributed to cerebral vascular damage with symptoms related to central nervous system damage involving pyramidal, extrapyramidal, and pseudobulbar tracts. There are also reports of hypertension, renal damage, elevated cholesterol, and early arteriosclerosis. Some recovery from these effects is the rule, but such recovery is slow, occurring over months or years, and some paralysis may persist. There have also been reported effects on the reproductive system in infertility, and males having spermatic disorders.

Carbon disulfide is a very flammable substance; a steam pipe or even a hot radiator can ignite its vapors. It also has a very wide range of explosive concentrations and thus should not be exposed to heat, flame, sparks, or friction. Carbon disulfide reacts violently with aluminum, chlorine, azides, cesium azide, chlorine monoxide, ethylene diamine, ethyleneimine, fluorine, lithium azide, nitric oxide, nitrogen tetroxide, sulfuric acid plus permanganates, potassium, potassium azide, rubidium azide, zinc, and various other oxidizing agents. When carbon disulfide is used to desorb organic materials from activated charcoal, as in the case of air sample analysis, a significant amount of heat can be liberated.

OSHA regulations require that worker 8-hour time-weighted average exposures not exceed 20 ppm; ceiling levels of 30 ppm are acceptable to the point that the 8-hour TWA is not exceeded, and additional peak exposures up to 100 ppm for no more than 30 min are allowable. ACGIH has decreased (1980) the 8-hour time-weighted average exposure to 10 ppm and has noted that skin absorption can significantly contribute to toxic effect.

Gloves and protective apparel should be used when handling liquid carbon disulfide. As much as possible, laboratory operations should be confined to a hood that has protection factors high enough to prevent significant exposure or to closed systems.

6.5.6 Carbon Monoxide

Carbon monoxide is a direct and acutely cumulative poison. It combines with the hemoglobin of the blood to form a relatively stable compound (carboxyhemoglobin) rendering it useless as an oxygen carrier. However, the effect can be reversed over time when the victim breathes only clean air. When about one-third of the hemoglobin has entered into such combination with carbon monoxide, the victim dies. Since carbon monoxide is odorless, colorless, and tasteless, it has no warning properties. Exposure to 1500-2000 ppm carbon monoxide 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 carbon monoxide poisoning, but occasionally the first evidence of poisoning is the collapse of the patient. Pregnant women are more susceptible to the effects of carbon monoxide exposure.

Carbon monoxide should be used only in areas with adequate ventilation employing the general procedures outlined in Chapter 6.3 A trap or vacuum break should always be used to prevent impurities from being sucked back into a carbon monoxide cylinder.

6.5.7 Carbon Tetrachloride

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

The acute toxicity of carbon tetrachloride by all routes of exposure is low to moderate (oral LD_{50} in rats is 2,350 mg/kg). Carbon tetrachloride shows carcinogenic effects in animal studies and is listed in group 2B ("possible human carcinogen") by IARC.

In cases where carbon tetrachloride has to be used, then the general procedures outlined in Chapter 6.3 should provide adequate protection. All operations should be carried out in a fume cupboard, not only because of the carcinogenicity of the substance, but also because of its other toxic effects (e.g., hepatotoxicity) and its volatility. Nitrile rubber is the recommended material for gloves and other protective clothing.

6.5.8 Chlorine

Chlorine is a severe irritant of the eyes, skin, and mucous membranes. Inhalation may cause coughing, choking, nausea, vomiting, headache, dizziness, difficulty breathing, and delayed pulmonary edema which can be fatal. Exposure to ca. 500 pm for 30 minutes may be fatal and 1000 ppm can be lethal after a few breaths. Chlorine is highly irritating to the eyes and skin; exposure to 3-8 ppm causes stinging and burning of the eyes, and contact with liquid chlorine or high concentrations of the vapor can cause severe burns. Chlorine can be detected by its odor below the permissible limit; however, because of olfactory fatigue, odor may not always provide adequate warning of the presence of harmful concentrations of this substance. There is no evidence for carcinogenicity or reproductive or developmental toxicity of chlorine is humans. The LC_{50} for inhalation (rat) is 293 ppm (1 h); the PEL (permissible exposure limit) is 1 ppm while the TLV-TWA (threshold limit value - time-weighted average) is 0.5 ppm.

Chlorine is noncombustible but is a strong oxidizer and will support combustion of most flammable substances, sometimes with explosive violence. Cylinders of chlorine should be stored in locations appropriate for compressed gas storage and separated from incompatible compounds such as hydrogen, acetylene, ammonia, and flammable materials. Because of its high toxicity, *laboratory operations using chlorine must be carried out in a fume cupboard employing the general procedures outlined in Chapter 6.3*

6.5.9 Chloroform

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

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

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

The current OSHA PEL (permissible exposure limit) for chloroform is 50 ppm as an 8-hour time-weighted average. This standard is also a ceiling level that should not be exceeded for any 15-min period. The ACGIH currently recommends that chloroform be treated as a suspect human carcinogen and recommends an 8-hour time weighted average exposure of 10 ppm.

If chloroform has to be used, the general procedures outlined in Chapter 6.3 should provide adequate protection. The high volatility of chloroform emphasizes the importance of a fume cupboard for such operations. Polyvinyl alcohol gloves provide the best hand protection.

6.5.10 Dimethyl Sulfate (DMS) and Diethyl Sulfate

The use of dimethyl and diethyl sulfates requires prior approval from the Chemistry Safety Committee. (Chapter 8).

Many cases of dimethyl sulfate poisoning have been reported. The common initial symptoms are headache and giddiness, with burning of the eyes. The patient's condition may worsen, with painful eyes, nose and throat irritation, loss of voice, coughing, difficulty in breathing and swallowing, vomiting, and diarrhea possible. The onset of the symptoms may be delayed up to 10 hours. This substance is extremely hazardous because of its lack of warning properties and its delayed toxic effects. Skin contact causes blistering and necrosis, and DMS can be absorbed through the skin in sufficient quantity to cause systemic intoxication. In the worst cases, there is severe inflammation of the mucous membranes and pulmonary injury that may be fatal; several deaths have occurred. For example, exposure to 97 ppm for 10 min was fatal. DMS is moderately toxic to animals via the oral route: 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 (threshold limit value) for DMS is 0.1 ppm (0.5 mg/m^3) as an 8-hour time-weighted average. DMS is classified as being suspected of carcinogenic potential in humans by the ACGIH. The OSHA PEL (permissible exposure limit) for DMS is 1.0 ppm. These limits include a warning of the potential contribution of skin absorption to the overall exposure.

The general procedures outlined in Chapter 6.4 should be used when handling more than a few grams of DMS in view of its fairly high carcinogenic potency in rats by inhalation and its ability to penetrate the skin.

It is particularly important to avoid skin contact by the appropriate use of rubber gloves, a rubber apron, and other protective apparel, and to avoid inhalation of even low concentrations of vapor by working in a fume cupboard. Operations involving smaller quantities of DMS can be conducted using the general procedures presented in Chapter 6.3.

6.5.11 Ethylene Dibromide (1,2-Dibromoethane)

Ethylene dibromide (EDB) is classified as a compound with a moderate degree of acute toxicity; the approximate oral lethal dose of EDB for humans is 5-10 mL. Skin absorption of EDB can also cause death, and inhalation of the vapor can produce pulmonary edema. EDB can cause severe irritation to all exposed tissues, respiratory tract, skin, and eye. Systemic effects include central nervous system depression, kidney injury, and severe liver necrosis. Ethylene dibromide is highly toxic to animals via inhalation. The maximum survival exposure of rats to EDB vapors in air are 3000 ppm for 6 min, 400 ppm for 30 min, and 200 ppm for 2 hours. It is moderately toxic via the oral and skin routes; LD_{50} (rats, oral) = 108 mg/kg; LD_{50} (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 fore-stomach) in mice and rats following oral administration. The 1979 TLV (threshold limit value) for EDB was 20 ppm (155 mg/m^3) as an 8-hour time-weighted average. The exposure limit is 30 ppm over any 15-min period. These limits include a warning about the potential contribution of skin absorption to the overall exposure. In 1980, the ACGIH put EDB in category A 1b (human carcinogen). For this category, there is no assigned TLV (threshold limit value), but the ACGIH recommends that those working with A1b carcinogens should be properly equipped to ensure virtually no contact with the carcinogens. The OSHA PEL (permissible exposure limit) for EDB is 20 ppm, and the acceptable maximum peak is 50 ppm for 5 min in any 8-hour time period.

On the basis of the carcinogenicity data for EDB, *the procedures described in Chapter 6.4 should be followed when handling more than a few grams in the laboratory.*

Operations involving smaller quantities can be carried out using the procedures outlined in Chapter 6.3. Serious skin injury can occur from direct exposure to EDB. The substance can penetrate neoprene and several other types if plastic. Therefore, gloves and other protective apparel made of these materials provide only temporary protection if EDB spills on them.

6.5.12 Hydrazine

Hydrazine is classified as a compound with a high degree of acute toxicity; exposure to its vapors can cause respiratory tract irritation, excitement, convulsion, cyanosis, and decrease in blood pressure. The liquid can severely burn the eyes and skin. Hydrazine can cause fatty degeneration of the liver, nephritis, and hemolysis. Hydrazine also poses a dangerous fire and explosion risk and can explode during distillation if traces of air are present. Hydrazine is moderately toxic to animals via the inhalation, oral, and skin routes: LC_{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 5-47 times, the dogs showed liver damage, with lesser damage to the kidneys and lungs, while the guinea pigs had pneumonitis and partial lung collapse. Hydrazine is not regarded as having adequate warning properties.

Hydrazine and hydrazine salts have been shown to be carcinogenic in mice after oral and intraperitoneal administration and in rats following oral dosing. By the oral route, effects were found at doses of 24-36 (mg/kg)/day in mice and 20 (mg/kg)/day in rats. No tumors were observed in Syrian golden hamsters after oral administration. The

ACGIH has classified hydrazine as suspected of carcinogenic potential in humans. The TLV (threshold limit value) for hydrazine is 0.1 ppm (0.1 mg/m^3) and the OSHA PEL (permissible exposure limit) is 1.0 ppm (1 mg/m^3) 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 of 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 Chapters 6.3 and 6.4 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.

6.5.13 Hydrogen Bromide and Hydrogen Chloride

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

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

Operations involving significant quantities of hydrogen bromide and hydrogen chloride should be conducted using the general procedures outlined in Chapter 6.3.

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).

Note that several lachrymatory compounds generate HCl or HBr upon contact with human tissue. The most volatile of such compounds pose a major risk in a chemical spill scenario. Some common volatile lacrymators fitting this description are listed below:

Acetyl chloride
Acetyl bromide
Other low molecular weight acid halides
Phosphoryl chloride
Thionyl chloride
Titanium tetrachloride

6.5.14 Hydrogen Cyanide

Immediate and prior approval from the Chemistry Safety Committee is required before each operation using hydrogen cyanide (see Chapter 8).

6.5.15 Hydrofluoric Acid/Hydrogen Fluoride

The use of dilute or concentrated hydrofluoric acid or anhydrous hydrogen fluoride requires immediate and prior approval from the Chemical Safety Committee (See Chapter 8).

All forms - dilute or concentrated solutions or the vapor - of hydrofluoric acid (HF) cause severe burns. Inhalation of anhydrous HF or HF mist or vapors can cause severe respiratory tract irritation that may be fatal. Death from pulmonary edema occurred within 2 hours in three of six workers splashed with 70% HF solution despite prompt showering with water. Anhydrous HF is a clear, colorless liquid that boils at 19.5 °C. Because of its low boiling point and high vapor pressure, anhydrous HF must be stored in pressure containers. A 70% aqueous solution is a common form of HF. Hydrofluoric acid is miscible with water in all proportions and forms an azeotrope (38.3% HF) that boils at 112 °C. Anhydrous or concentrated aqueous HF causes immediate and serious burns to any part of the body. Dilute solutions (<30%) and gaseous HF are also harmful, although several hours may pass before redness or a burning sensation is noticed. These burns may still be quite severe and progressively damaging to the skin and deeper tissues. Undissociated HF readily penetrates skin and deep tissue where the corrosive fluoride ion can cause necrosis of soft tissues and decalcification of bone; the destruction produced is excruciatingly painful. Fluoride ion also attacks enzymes (e.g., of glycolysis) and cell membranes. The process of tissue destruction and neutralization of the hydrofluoric acid is prolonged for days, unlike other acids that are rapidly neutralized. Because of the insidious manner of penetration, a relatively mild or minor exposure can cause a serious burn "[Proctor, N. H.; Hughes, J. P.; Fischman, M. L. *Chemical Hazards of the Workplace,* J. B. Lippincott Co., Philadelphia, 1988, p.279]. Occasionally workers fail to recognize the importance of seeking medical attention for HF burns *before* pain commences. By the time the victim is affected with progressively deep and more painful throbbing and burning, serious damage may have taken place. Exposures under fingernails can be a particularly painful problem if ignored. Wearing clothing (including leather shoes and gloves) that has absorbed small amounts of HF can result in serious delayed effects such as painful slow-healing skin ulcers.

When handling HF, it is crucial to ensure adequate ventilation by working only in a fume cupboard so that safe levels (3 ppm) are not exceeded.

All contact of the vapor of the liquid with eyes, skin, respiratory system, or digestive system must be avoided by using protective equipment such as a face shield and neoprene or polyvinyl chloride gloves.

The protective equipment should be washed after each use to remove any HF on it. Safety showers and eyewash fountains should be nearby. Anyone working with HF should have received prior instructions about its hazards and in proper protective measures and should know the recommended procedure for treatment in the event of exposure (Reinhardt, C. F. et al.; *Am. Ind. Hyg. Assn. J.*, **1966**, *27*, 166).

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

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

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

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

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

6.5.16 Hydrogen Sulfide

The use of hydrogen sulfide requires prior approval from the Chemistry Safety Committee. (Chapter 8).

The acute toxicity of hydrogen sulfide by inhalation is moderate. A five minute exposure to 800 ppm has resulted in death. Inhalation of 1000 to 2000 ppm may cause coma after a single breath. Exposure to lower concentrations may cause headache, dizziness, and nausea. Low concentrations (20-150 ppm) of hydrogen sulfide can cause eye irritation which may be delayed in onset. Although the odor of hydrogen sulfide is detectable at very low concentrations (below 0.1 ppm), it rapidly causes olfactory fatigue at higher levels, and therefore is not considered to have adequate warning properties. Hydrogen sulfide has not been shown to be carcinogenic or to have reproductive or developmental effects in humans. The hydrogen sulfide LC_{50} for inhalation (rat) is 444 ppm; the PEL (permissible exposure limit) *ceiling* is 20 ppm, and the TLV-TWA (threshold limit value - time-weighted average) is 10 ppm. Hydrogen sulfide is flammable in air, and the combustion products are also toxic by inhalation. It is incompatible with strong oxidizers, will attack many metals, some plastics and rubbers, and reacts violently with a variety of metal oxides. *Laboratory operations with hydrogen sulfide should be carried out in a fume cupboard using the general procedures outlined in Chapter 6.3* In particular, cylinders of hydrogen sulfide should be stored and used in a continuously ventilated gas cabinet or fume cupboard.

6.5.17 Nickel Carbonyl

The use of nickel carbonyl requires prior approval from the Chemistry Department Safety Committee (see Chapter 8).

6.5.18 Nitric Oxide

Nitric oxide (NO) does not exist as such in significant quantities in atmospheric air, but in the presence of oxygen, is transformed into nitrogen dioxide, a very toxic substance (see directly below).

6.5.19 Nitrogen Dioxide

The use of nitrogen dioxide requires prior approval from the Chemistry Safety Committee. (Chapter 8).

Nitrogen dioxide (NO_2) is classified as a highly acute toxin; it is a primary irritant, acting principally on the lungs and to a lesser extent on the upper respiratory tract. It is certainly one of the most insidious of the gases. The inflammation of the lungs may cause only slight pain, but the edema that results may easily cause death. Toxic effects may develop after a 10 minute exposure to 10 ppm, and one hundred ppm of NO_2 in air is a dangerous concentration for even a short exposure. Exposure to 200 ppm for 1-2 min may be fatal.

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

Nitrogen dioxide should be handled using the general procedures outlined in Chapter 6.3. 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.

6.5.20 Mercury

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

Mercury poisoning from exposure by chronic inhalation produces a variety of symptoms. The characteristic effects are emotional disturbances, unsteadiness, inflammation of the mouth and gums, general fatigue, memory loss, and headaches. Kidney damage may result from poisoning by 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 Chapter 6.3 should be followed when working with large quantities of liquid mercury. Every effort should be made to prevent spills of metallic mercury because the substance is extremely difficult and time consuming to pick up. Droplets get into cracks and crevices, under table legs, and under and into equipment. If spills are frequent and Hg is added to the general air level, the combined concentration may exceed the allowable limits.

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

Cleanup of spills - Pools of metallic Hg can be collected by suction by using an aspirator bulb or a vacuum device made from a filtering flask, a rubber stopper, and several pieces of flexible rubber and glass tubing. Alternatively, mercury-spill cleanup kits are available commercially. When a large spill, pressure system rupture, or heating of mercury is involved, the HSEO must be consulted 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 cleanup activities, and broken thermometers containing small amounts of residual mercury, should be placed in a sealed plastic bag, labeled, and disposed of in a safe manner.

6.5.21 *N*-Nitrosodialkylamines and Certain Other *N*-Nitroso Compounds

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

The general procedures outlined in Chapter 6.3 & 6.4 should be followed when working with N-nitrosodialkylamines. All work with *N*-nitrosodialkylamines should be carried out in a well-ventilated fume cupboard 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 fume cupboard).

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

6.5.22 Phosgene

The use of phosgene requires prior approval from the Chemistry Safety Committee. (Chapter 8).

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

Laboratory operations involving phosgene require the use of the general procedures outlined in Chapter 6.3

Work with phosgene should always be carried out within a fume cupboard. 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 (white crystalline solid, MP 79 °C, Aldrich 33,075-2).

6.5.23 Sodium Cyanide (and other cyanide salts)

Inorganic cyanide salts are classified as substances with a high degree of acute toxicity. Sodium cyanide is among the fastest acting of all known poisons. The lethal oral dose for humans is 200 mg. The symptoms of cyanide overdose include weakness, headache, confusion, and, occasionally, nausea and vomiting. Higher doses may be followed by almost instantaneous death. Solutions are irritating to the skin, nose, and eyes, and cyanide is absorbed through the skin. Sodium cyanide is highly toxic to animals via the oral route: LD_{50} (rats) = 6.4 mg/kg. It can be corrosive to the skin and the eyes, for it is highly alkaline. Sodium cyanide can also produce toxic symptoms via skin absorption and inhalation. The TLV (threshold limit value) and the OSHA PEL (permissible exposure limit) for cyanide are both 5 mg/m^3 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^3 limit be retained but that its basis be changed from an 8-hour TWA to a 10-min ceiling.

Security (ext. 8999) should be contacted immediately and the cyanide antidote should be administered.

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 Chapter 6.3.* 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 Safety Office to arrange disposal of these containers.

In the event of exposure

Anyone who has been exposed to HCN should be removed from the contaminated atmosphere immediately, if it is judged safe to perform a rescue operation. Security (ext. 8999) should be contacted immediately and the cyanide antidote should be administered. Any contaminated clothing should be removed and the affected area deluged with water. Emergency medical attention should be obtained immediately.

7.0 Proper Planning of Laboratory Work

Hazardous chemical reactivity and human health hazards are inherent in research. In the normal course of work, a researcher is often working with chemicals having undetermined or incompletely evaluated properties, or with familiar materials in a new chemical environment that might lead to an unexpected reaction.

Proper planning will, however, allow each researcher to decrease the occurrence of unexpected events and minimize the possibility of personal injury. Proper planning incorporates the known and anticipates the unexpected.

7.1 Recognition and Assessment

The first step in proper planning is recognition and assessment of the physical, chemical, and health hazard properties of each chemical and combination of chemicals that will be used.

Some of the important factors that must be considered include:

7.1.1 Physical Properties

a. Vapor pressure?
b. Boiling point?
c. Flash point?
d. Auto-ignition temperature? At what pressure?
e. Explosion limits in air? At what temperature?
f. Are the quantities such that a pre-start-up inspection by your supervisor is required? (See Chapter 8.2)

7.1.2 Chemical Reactivity

a. Will it form peroxides? (consult Table VIII in Chapter 5.3.2)
b. Is it a strong oxidizing or reducing agent?
c. Will it react violently with water?
d. Will it decompose spontaneously?
e. How is it affected by heat, light, pressure, *etc*.?
f. Will it react exothermically with any other types of material?
g. Are any of the compounds in use potentially explosive? (consult Table VI in Chapter 5.1.8)

7.1.3 Hazards arising from the Interaction of Reagents

Each researcher must evaluate the properties of every potential combination of chemicals that could occur in the work:

a. Are there any possible *incompatibilities* between your reagent(s) and/or reagent(s) and solvent? (consult Table IX in Chapter 5.3.4)
b. Could any undesirable byproducts be formed?
c. Is the material's composition certain?
d. What are the consequences of inadequate mixing?
e. What is the heat of reaction?

7.1.4 Health Effects

a. Is it corrosive, an irritant, a sensitizer?
b. Is it carcinogenic? (consult Table II in Chapter 5.1.1 and/or Table X in Chapter 6.1.1)
c. Is it a reproductive or developmental hazard? (consult Table III in Chapter 5.1.2)
d. Is it a hazard to a particular organ? (Chapter 5.1.6)
e. Does it possess acute or chronic toxicity?
f. Based on the potential health risks of accidental exposure, is a Pre-Start-Up Inspection by your supervisor advisable?

7.2 Planning for the Unexpected. WHAT COULD GO WRONG?

The second step in proper planning is to answer the question:

What is the worst possible event or series of events that could occur?

For example, what would happen if...

Chemical fume hood ventilation fails?
Electric power fails?
Cooling water fails?
Refrigeration fails?
Instrument air fails?
The reaction overheats?
The reaction over-pressurizes?
Water leaks into the process?
A condenser plugs up?
Seals fail?
Agitation (stirring) is lost?
Too much of a reactant is added?
A spill occurs?

7.3 Site Selection

The final step is to plan the scale and physical location of the work so that *even in the worst conceivable scenario, no significant damage or personal injury would be possible*.

For some chemical operations, merely performing them in the fume cupboard will not offer sufficient protection. When in doubt, place a blast shield between the reaction and the fume cupboard sash window.

In the case of permanent installations of fragile equipment that are not housed in a fume cupboard (for example solvent stills or vacuum lines), in some cases it is advisable to build a 3-side plexiglass enclosure to mitigate the risk to the equipment, and to workers nearby to this equipment.

7.4 Lab Self-Inspection

The checklist below is based on HSEO's published "Laboratory Safety Self-Survey Checklist (http://www.ab.ust.hk/sepo/tips/ls/ls000.htm)

7.4.1 Housekeeping

_____ Facility, furniture, work areas, sinks and equipment are generally clean
_____ Items not in use are stored away
_____ Door viewing panel not covered or blocked
_____ Adequate aisle space within the laboratory
_____ Overhead storage is secure and minimized
_____ No storage of hazardous materials on open shelves above the bench
_____ Workbench, chairs, ladders, footstools are in good condition
_____ Exits not blocked
_____ Work area separated from study or social areas

7.4.2 General Laboratory Safety

_____ Accurate Hazard Warning Placard posted at entrances
_____ Laboratory secured against unauthorized entry
_____ Warning labels on refrigerator and freezer (Radioactive, Biohazard, etc)
_____ Warning signs and labels at designated work areas (Radioactive, Carcinogens, etc)
_____ HKUST Safety Manual available
_____ Lab-specific MSDS collection available
_____ Safety training arranged and provided for workers
_____ Unattended experiments labelled with hazards and contact name and telephone
_____ Equipment maintained in good condition, preventive maintenance program in place
_____ Current Operational Safety Procedures (OSP) in place for hazardous equipment and operations
_____ No food or drink in the Laboratory.

7.4.3 Personal Practices

_____ Lab coats and safety glasses worn by all
_____ Proper gloves are used as needed
_____ Other personal protective equipment used properly as needed
_____ No inappropriate clothing and shoes (shorts, sandals, slippers etc).
_____ Long hair properly restrained
_____ Gloves removed before handling telephone, door handle or leaving laboratory
_____ No mouth pipetting

_____ No eating or drinking in work area

7.4.4 Chemical Storage And Handling

_____ Current chemical inventory present
_____ No excessive chemical stock
_____ No expired chemicals
_____ Chemical containers properly labeled
_____ Synthesized chemicals adequately labeled.
_____ All chemical containers in good condition and closed properly
_____ Only compatible chemicals are stored together
_____ Polyethylene trays for separate storage of acids and bases
_____ Secondary containment for stored chemicals as necessary
_____ Highly toxic or carcinogenic chemicals identified and properly stored.
_____ Designated work area for particularly hazardous chemicals.
_____ Peroxide formers dated upon receipt and opening, and not stored beyond expiration
_____ Flammable liquids stored in flammable cabinet or explosion-proof refrigerator
_____ Flammable liquids stored away from sources of heat and ignition

7.4.5 Compressed Gas Cylinders

_____ Gas cylinders secured to structural component of the building
_____ Gas cylinders stored in protected, well ventilated, and dry locations away from heat and combustible materials
_____ Compressed gas cylinders fitted with appropriate flow regulators
_____ Gas tubing of suitable material and pressure rating secured and in good condition
_____ Protective caps in place when not in use for toxic or corrosive gas cylinders
_____ Labels attached and show correct use status
_____ Flame arrester installed in supply line of flammable gas
_____ Acetylene cylinder maintained at upright position and copper tubing not used

7.4.6 Hazardous Waste Management

_____ Specific liquid chemical waste containers used
_____ Waste containers in good condition and kept closed
_____ No more than 50 liters of hazardous waste stored in the laboratory

_____ Waste log sheet available and properly filled in after each addition of waste
_____ Secondary containment for liquid chemical waste
_____ Broken glass/sharps containers are used
_____ No intentional disposal of chemicals by evaporation into a fume hood

7.4.7 Laboratory Fume Hood And Ventilation

_____ Certification current (check sticker on front panel)
_____ Green pilot air flow indicator lamp properly functioning
_____ Storage within the hood minimized and containers kept sealed
_____ Front sash at appropriate level when hood is in use / not in use
_____ Low-velocity warning alarm functions properly
_____ Biological Safety Cabinet certification current (check sticker on front or side)
_____ "DO NOT USE" sign for hood not in working condition
_____ All work generating vapor, fume, or aerosol performed in fume hood
_____ Fume generating apparatus at least 20 cm from face of hood
_____ Local exhaust units used where hoods are not suitable
_____ Negative pressure in laboratory not disturbed by constantly opened door or ceiling tile
_____ Ventilation inlets and outlets not blocked

7.4.8 Radiation Safety

_____ All radiation workers registered with HSEO
_____ Thermoluminescent Dosimeter (TLD) worn by all radiation workers
_____ Current radioactive material inventory available
_____ Radioactive material properly stored and locked
_____ Sufficient shielding for radiation work available
_____ Calibrated radiation survey meters available
_____ Periodic facility contamination evaluation performed and documented
_____ Radioactive wastes properly stored, according to physical forms and radionuclides
_____ Radioactive waste log sheet filled out properly

7.4.9 Electrical Safety

_____ All electrical circuits are three-wire with earths
_____ High voltage equipment (>600 V) labeled, grounded, and insulated
_____ Live electrical parts adequately insulated or enclosed

_____ Electrical control panels/switches not obstructed
_____ Extension cords not used as permanent wiring
_____ Proper wiring and plugs (3-prong of appropriate standard)
_____ No circuits overloaded with extension cords or multiple connections
_____ Apparatus equipped with earths or double insulated
_____ Heating apparatus equipped with redundant temperature controls

7.4.10 Emergency Preparedness

_____ Emergency procedures and Fire Escape Route posted
_____ Emergency 8999 number sticker on telephone set
_____ Antidotes available if hydrofluoric acid is used
_____ First aid materials available and in good condition
_____ Emergency ventilation switch accessible and functional
_____ Chemical spill kit and cleanup procedures available if considered necessary by departmental plan
_____ Training in spill clean-up procedures provided and documented when appropriate
_____ Safety showers and eye washes easily accessible
_____ Safety showers and eye washes inspected monthly (see tag)
_____ Fire extinguishers, blankets and sand available
_____ Fire extinguisher inspected within one year (see tag)
_____ Type D fire extinguisher (blue colour) available if potential of metal fire exists
_____ 600mm vertical clearance maintained from sprinkler heads
_____ Two well-separated exits, doors swing outward, for hazardous laboratories
_____ Hazardous materials not stored along exit route
_____ Exit signs readily visible

7.5 General Guidelines for Performing Large Scale Reactions

Large scale reactions present a significant safety hazard and require additional planning before they are carried out. Although there is no universally agreed-upon definition of the term "large-scale", in the ensuing discussion "large-scale" will be taken to mean any reaction carried out in a 500mL or larger flask. Note that a "Pre-Start-Up Inspection" by your supervisor may be required before beginning such a reaction. See Chapter 8.2 for important details.

7.5.1 Scale up guidelines

Two general guidelines should be given regarding large scale reactions:

1. Unless you are an extremely experienced synthetic chemist *and* are following a very detailed large scale synthetic procedure (such as an *Organic Syntheses* procedure), reactions should *always* be performed on a small scale first.

2. After successfully performing the small scale reaction, subsequent reactions should be scaled up by a *maximum* of a factor of five. The same procedure which works wonderfully on a one-gram scale may be hazardous or chemically non-selective on a ten-gram scale. The major factors that present problems in scale-up are heat transfer rate and inefficient mixing. Either of these can lead to a run-away exotherm which might result in sudden escape of the reagents from the apparatus, or in the worst case, explosion or fire.

Remember that the rate of heat transfer will be proportional to the exposed surface area of the flask. Because volume is a function of r^3, and surface area is a function of r^2, the overall efficiency of heat transfer decreases as 1/r. Thus the efficiency of heat transfer from a 1 liter flask is only one-tenth of that of a 100 mL flask.

7.5.2 Performing Highly Exothermic Reactions

When performing highly exothermic reactions on a large scale, such as addition of a Grignard reagent to a metal or nonmetal halide, it is optimum to select the reaction temperature and addition rate in such a way that the reactive reagent is consumed *immediately* upon addition. Performing reactions at room temperature with a reflux condenser is especially useful in this regard as the rate of reflux is indicative of the rate of reaction. If for reasons of selectivity the reaction cannot be performed above room temperature, then reaction at 0 °C is greatly preferable to reaction at -78 °C. *There is great danger in performing highly exothermic reactions at too low a temperature.* If a reaction is performed at "too cold" a temperature, unreacted reagent may build up in the reaction flask (the so-called induction period); as reaction finally begins the temperature rises, leading to an exponential increase in the rate of reaction and concurrent heat generation. If enough reagent is present in the flask the cooling capability of the low temperature bath will be surpassed, and explosion will result. Such an incident resulted in terrible injuries to a graduate student from the California Institute of Technology in the 1980's.

7.5.3 Know the Identity and Quantity of the Major Reaction Byproducts

Accidents often result from a researcher's failure to consider the identity of the major reaction by-products. Good notebook writing habits can mitigate this danger.

Balance your equations! When performing reactions with pyrophoric or water-reactive materials calculate the molar amount of reagent (or derivative) remaining after the reaction; then cautiously add 1.5 - 2.0 times the amount of material needed to "kill" the excess reagent before opening the flask to the atmosphere.

7.5.4 Gas Generation During Reaction or Workup

If one of the reaction byproducts is a gas, ensure that openings in the reaction flask are large enough to avoid a catastrophic pressure build-up. If the gas is corrosive or toxic, *it must be efficiently scrubbed*. It is not acceptable to simply let these gases go up the fume cupboard. For example hydrogen chloride gas can be scrubbed by passing through a solution of sodium hydroxide. A recommended gas-scrubbing apparatus is described in Vogel's *Textbook of Practical Organic Chemistry*, 5th Edition (1989) p. 85-86.

Gas evolution may be accompanied by considerable frothing or foaming; in some cases this may lead to sudden escape of the contents of the flask. Excellent agitation is a must; a mechanical stirrer with the largest paddle available is recommended. Secondary containment is advisable in planning for all large scale reactions and is especially worthwhile in the case of gas evolution. Note that the maximum rate of "stable" gas evolution is related to the area of the exposed surface of the reaction. This ratio of this area to the volume of a reaction decreases as a function of r, the radius of the flask. Thus the same procedure used to perform a reaction in a 100 mL flask may be nearly impossible to use on a 1-liter scale.

When quenching hydride reagents the use of acetone or ethyl acetate is vastly preferred to the use of proton sources. Use of these reagents obviates the generation of hydrogen gas, and thereby mitigates the risk of explosion, fire and loss of containment.

7.6 Operational Safety Procedures (OSPs)

According to the University *Safety and Environmental Protection Manual* the following activities require that a detailed OSP be written out and approved by HSEO before starting work:

- Operation of an experimental high-energy system (large electric current, high magnetic field, high-pressure gas, high voltage, **laser systems**, etc.)
- Operation of equipment capable of generating significant levels of hazardous radiation.
- Any activity that involves the presence of a radioactive material in a facility not already approved for the material.
- Any activity that involves the use of a carcinogen, suspect carcinogen, or etiological agent (pathogen) in a facility not already approved for the material.
- Any activity where implementation of the controls specified by a prescribed code or standard is not sufficient to reduce the risk to an acceptable level.
- Any activity that is not in compliance with a mandatory code or standard of an existing safety policy.
- Whenever required by management or by the Safety and Environmental Protection Manual.

For details on OSP consult Chapter 2, page 2 of the University *Safety and Environmental Protection Manual*.

Operational Safety Procedure Preparation Guide

1. General

Briefly describe the nature of the operation and its objective. Name the responsible parties. State the area to be controlled and the type and range of work authorized by the OSP.

2. Responsibilities

State who in management is responsible for implementing the controls specified by the OSP and all other applicable safety standards, and for the overall safety of this operation. Also provide the name of an alternate or alternates.

3. Hazards Analysis

Include the following information:

- State why this OSP is being issued.
- Describe the hazards associated with this operation that would have an unacceptable risk without the additional controls described in this OSP. Briefly describe how the anticipated controls described in this OSP will reduce the risks to an acceptable level.
- List any hazardous materials and equipment to be used and the properties of concern if this information is not readily available.
- Discuss the effects, if any, on the environment and how they are being controlled.

4. Controls

Material Controls

State the limits on the quantity, pressure, temperature, concentration, etc. that are vital to the control of the hazardous materials involved. Describe the controls on shipping, receiving, storage, and disposal as well as the monitoring program, and the handling of contaminated wastes.

Equipment Controls

Present a sequential description of the proposed operation with enough detail to permit reviewers and approvers to understand what will be going on. Include a description of any equipment and built-in safety features; state limits on temperature, pressure, voltage, etc. and indicate the safety and environmental monitoring required.

Personnel Controls

Describe the necessary training for personnel involved in the operation. Describe the access restrictions to be implemented. List the protective equipment required and tell how it will be provided. State any special personal dosimeter exchange cycle requirements.

Emergency Controls

Outline actions to be taken during an emergency. This plan of action must be sufficiently detailed to serve as an effective guide for emergency response personnel. It may be issued as a separate appendix.

5. Appendices

Appendices may be included as part of the OSP when supplementary information is needed. They generally do not require a separate authorizing signature. Examples are as follows:

Appendix A - Emergency Call-Out List

This list should include names and phone numbers of individuals who would be needed to respond to or control the emergency, should one occur.

Appendix B - Building Floor Plan or Area Layout

This plan should show the location of possible hazards, exits, preferred evacuation routes, location of vital utility controls, etc.

Appendix C - Special Operating Instructions

An operating procedure should be written for unusually hazardous operations. Preparation of such procedures is particularly helpful when the operational steps are numerous or complicated.

Appendix D - Detection and Alarm Plan

This plan should describe the special detection and alarm systems in the facility. Reference should be made to other sources of information such as schematics and drawings. Typical topics are fire detection and suppression systems (if other than standard), criticality alarms, hazardous material alarms, and evacuation alarms.

Appendix E - Material Safety Data Sheets (MSDS)

MSDS should be provided for any and all hazardous materials to be used in the operations and should be detailed enough to provide information concerning exposure limits, health effects, fire and spill containment, and proper disposal.

For sample OSP, please visit http://www.ab.ust.hk/sepo/sm06/app/OSP.JPG

8.0. Prior Approval Requirements

8.1 Restricted Chemicals Requiring Prior Approval

The use of certain particularly hazardous substances requires the prior approval of the Chemistry Department Safety Committee. At the time of this writing, prior approval is required for work with the compounds listed below. Additions to this list will be posted in the Chemistry Department Library of Laboratory Safety (Rm. 7127).

Dimethyl and diethyl sulfates
Fluorine
Hydrogen cyanide and cyanide salts
Hydrogen fluoride (anhydrous; dilute or concentrated hydrofluoric acid)
Hydrogen sulfide
Nickel carbonyl
Nitrogen dioxide
Phosgene
Radioactive substances

Researchers intending to work with one of these restricted chemicals must prepare an OSP (signed by their research supervisor) for review by the Safety Committee *well before* beginning work. 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.

4. 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.

8.2 Pre-Start Up Inspection

A "Pre-Start Up Inspection" is required whenever a reaction employing

1. 1 L or more of a flammable solvent; and/or

2. 50 grams of a particularly hazardous substance (PHS, see Chapters 6.1.1-6.1.3)

is performed for the *first* time. This inspection of the apparatus and procedure is carried out by the research supervisor in person *before* the reaction is carried out.

He/she will ensure that:

1. Proper containment is employed to mitigate the risk of chemical spill.

2. Ignition sources in the work area are minimized or eliminated (in the case of flammables).

3. That the reaction and workup procedures are well thought out in advance.

Note that general guidelines for performing large-scale reactions are given in Chapter 7.5.

9.0 Laser Safety

9.1 Introduction

Please refer to Chapter 11 ("Laser Safety") of the University Safety and Environmental Protection Manual *for a comprehensive presentation of Laser Safety issues. Note that this chapter is required reading for all laser users.*

The brief discussion given below is meant only to supplement the guidelines and regulations listed in the University Manual.

9.2 Laser Classification

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

9.3 Registration of Laser Equipment

9.3.1 Laser registration

All class III and IV lasers must be registered with HSEO before use. Details are given in Chapter 11 of the University *Safety and Environmental Protection Manual*. Part of the registration process involves writing an OSP. The OSP will be reviewed annually.

9.3.2 Laser inspection

Before any new class III and IV laser installation is cleared for use in experiments, it must be inspected and approved by HSEO.

Any major change in the experimental set-up of a class IIIa, IIIb or IV laser system, including moving the laser to a new location within HKUST, will require re-inspection by HSEO.

9.4 Registration of Personnel Working with Class IIIa, IIIb, or IV Lasers

No one is permitted to operate or to participate in an experiment utilizing any class IIIa, IIIb or IV laser without having fulfilled the requirements below. In addition, every laser user must obtain a laser eye examination (see below).

9.4.1 Laser Safety Course

All personnel whose work will involve the use of class IIIa, IIIb, or class IV lasers are required to attend the Laser Safety Course offered by HSEO. Attendance records will be maintained in the Chemistry Office.

9.4.2 Laser Eye Examination

All personnel whose work will involve the use of a class IIIa, IIIb or class IV lasers are required to obtain a laser eye examination before beginning work. It is the responsibility of the principal investigator to provide a list of all workers requiring a laser eye exam to HSEO. Laser users are also required to have an "exit" eye exam before leaving HKUST.

9.4.3 Authorization to Operate Specific Laser Equipment

No person is to operate any laser for which they have not been specifically "checked-out" by the research supervisor. A list of the types of lasers for which each researcher in a research group is checked out must be kept by the laboratory supervisor. A separate log book must be kept near each class III or IV laser. A list of qualified users must be attached to this logbook in an easily visible location. Every laser installation must have a sign mounted on each laser table indicating the type and power generated by the laser.

9.5 Procedures for the Safe Operation of Laser Equipment

The most common, though not life threatening injuries caused by lasers are permanent eye damage and severe skin burns. These injuries tend to be caused by poor safety habits, inadequate safety equipment being worn by the researcher, operator error, inadequate safety precautions around the laser, and inadequate preparation by the researcher. The risk to other non laser users in a laser laboratory can be greater than that to the laser user. A laser user must take responsibility for the safety of all workers in a laboratory. No beam manipulation procedure should be undertaken without explicit warnings to all workers and confirmation that the warning has been understood. It should be noted that almost all eye injuries involving lasers happen to personnel not wearing eye protection!!! In order to make the working environment around lasers as safe as possible and to minimize unforeseen events and to mitigate the effects of such events, the following safety procedures **must** be followed by all personnel operating or working around laser equipment.

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

2. Additional safety precautions must be followed for lasers emitting light other than visible, or experimental set-ups which convert visible laser light to the infrared or UV. To prevent accidental thermal burns and ignition of flammable materials, personnel or flammable materials must be kept out of the beam path. All beam stops/blocks

must be made with materials such as firebrick or blackened metals that do not give off specular reflections. IR or UV cards, to view the IR or UV laser beam respectively, must also be available. IR sensitive "Laser Watcher" paper is available from Showa Optonics Ltd, Tokyo Japan (IR-1: 0.9 -1.07 µm; IR-2: 1.48 - 1.55 µm; FAX 81-03-5450-5960). Acquisition of an "IR Viewer" may also be advisable to more easily detect stray IR.

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

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

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

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

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

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

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

10. When aligning laser beams, it is suggested to work at as low a power as possible. For example in the case of Q switched YAG lasers, it may be possible to turn off the Q

switching. The use of a video camera is strongly recommended if high power levels are necessary.

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

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

13. Wearing appropriate laser safety goggles/glasses will protect your eyes. However, there exist situations in which these goggles/glasses will *not* provide complete protection and eye damage will occur.

    Never look directly into a laser beam, even when wearing goggles/glasses!!!

    Goggles are designed to protect against momentary exposure and can bleach or melt if exposed to a direct beam (sometimes in a fraction of a second).

14. **Before** firing a YAG laser, check the water cooling system for the YAG rod.

15. **Before** firing an excimer laser, check the reservoir pressure.

16. The HCl and F_2 control valves of an excimer laser should be constructed from stainless steel.

9.6 Procedures to Prevent Electric Shock when Working with Lasers

Electric shock is the most life threatening hazard encountered in work with lasers. There have been several electrocutions of individuals in the U. S. from laser-related electrical accidents. These accidents could all have been prevented. Following the guidelines below should serve to significantly reduce the possibility of electric shock.

1. Unplug and ground power supplies.

2. Avoid wearing rings, metallic watchbands, and other metallic objects which could come into electrical contact with exposed wires, capacitors, etc.

3. When possible, use only one hand when working on a circuit. Keep the other hand in your pocket.

4. Assume that all floors are conductive when working with the high voltages that are commonly encountered with lasers.

5. Check that each capacitor is discharged, shorted, and grounded before allowing access to the capacitor area. An accidental discharge of capacitors of the size frequently found in laser power supplies into the body can be lethal. A proper manual grounding procedure for capacitors is the following:

   a. Check grounding stick resistance.
   b. Calculate discharge time.
   c. Ground for appropriate time with gloved hand.
   d. Measure voltage.
   e. Install Ground bar where practical.

   Even after having been disconnected and discharged, a capacitor may again build up an electrical charge. For this reason capacitors not in use should be grounded at all times.

6. Inspect capacitor containers for deformations or leaks.

7. Safety devices such as rubber gloves, insulating mats, and grounding connectors must be available and used when necessary.

8. Never work with a cyclotron tube without first measuring the voltage, even if the laser has been grounded.

9. **NEVER** work on a laser power supply or capacitors alone.

10. **NEVER** perform **any** work if doubt of personal safety exists.

10.0 Medical Surveillance

Researchers requiring advice on the health effects of chemicals involved in their work should consult the literature in the Chemistry Department Library of Laboratory Safety (Rm. 7127) and should consult HSEO for further assistance. Anyone who believes they may have been exposed to a hazardous substance (Chapter 5.1) should notify their supervisor immediately and contact the HSEO office. Individuals who experience any adverse health effects from exposure to hazardous substance should immediately report to the Campus Medical Clinic. Emergency assistance can be obtained by calling x8999. All accidents involving exposure to hazardous substances that require medical attention must be reported in writing, as part of the normal HSEO Accident/Incident report.

At the present time, HSEO insures that all respirator users, animal handlers, and biohazard substance users receive medical surveillance. They are required to have initial and periodic check-up by an Occupational Health (OH) physician. Implementation of a similar scheme for hazardous chemical users is currently in the planning stage.

Lab workers (and ideally, their supervisors) who anticipate extended work with *particularly hazardous substances (PHS)* should contact Dr. Samuel Yu of HSEO (ext. 6547) to set up an initial appointment to see the OH physician. As discussed in Chapter 6, PHS include substances of *high chronic toxicity* (such as known human carcinogens or reproductive/developmental toxins) and substances of *high acute toxicity*. Depending on the availability of suitable medical tests, a substance-specific surveillance plan will then implemented.

11.0 Biological and Radiation Safety

Because the work of most Chemistry department personnel does not routinely involve Biological or Radiation hazards, this section is rather brief. For further information see the University *Safety and Environmental Protection Manual* Chapter 9 ("Biological Safety") and Chapter 10 ("Radiation Safety").

11.1 Biological Safety

Precautions must be used when working with human or other primate tissues and bodily fluids. Such materials must be treated as being potentially infected with HIV, hepatitis viruses, or other pathogens. Work with such materials should be done according to the *Biosafety Level 2* protocol, which is outlined in detail in Chapter 9D of the University *Safety and Environmental Protection Manual.*

Human serum derived commercial products should be treated as infectious even it they have been screened for HIV and hepatitis. As a reasonable precaution person working with blood or blood products should keep their tetanus and hepatitis B vaccinations current.

11.2 Radiation Safety

Any work with radioactive substances requires prior approval from the Chemistry Safety Committee (see Chapter 8.1).

Before beginning any work with irradiating apparatus PIs must apply to HSEO for "Radiation Use Authorization (RUA)". Contact Dr. Joseph Kwan, Radiation Safety (HSEO) for further information.

Any person who will work with the X-ray diffractometer is required to take the *Sealed Sources and Irradiating Apparatus Course*. Upon completion they will be given a thermoluminescent badge (TLD) to wear when using the diffractometer. The TLDs must be returned every month and replacements will be issued every month. Reports on the exposure of each worker will be sent to Dr. Joseph Kwan (HSEO).

12.0 Hazardous Waste Management

12.1 Procedures for Disposal of Liquid Chemical Waste at HKUST

The following section is reproduced directly from materials provided by HSEO.

1. Introduction

With the implementation of the Waste Disposal (Chemical Waste) (General) Regulation, the disposal of chemical waste in Hong Kong is strictly controlled. Any unwanted substances that contain materials listed in Schedule I of the above regulation (refer to Appendix IV) are regarded as chemical waste. Enviropace Ltd, the contracted operator of the Chemical Waste Treatment Plant at Tsing Yi Island, provides central disposal Service for the waste collected by these procedures. A major difficulty in the handling of chemical waste in a tertiary institute such as HKUST is the relatively small quantities but large diversity in composition. This document provides general guidelines in the disposal of liquid chemical wastes. For enquiry about the disposal of chemical waste, please contact Mr. Edmond Cheng (ext. 6456) or fax to 2335 0074 of Safety and Environmental Protection Office (HSEO).

2. Service Scope

2.1 Spent chemical mixtures resulting from experiments and chemical analysis, surplus chemicals, and expired chemicals are collected under this scheme provided that 1) they meet the regulatory definition of "Chemical Waste" 2) they are in a liquid state and 3) they can be treated by the Chemical Waste Treatment Plant at Tsing Yi Island.

2.2. According to the Waste Disposal Regulation and guidelines of Environmental Protection Department, the following, as examples are *not* chemical wastes:

a. Neutralized salts that do not contain compounds listed in Appendix IV.
b. Apparatus rinsing water and wiping tissue with low chemical contents.
c. Elemental heavy metals in stable form (e.g. lead, copper, nickel).
d. Household chemicals used in laboratories for cleaning (e.g. soap, detergents).
e. Dilute acids and alkalis with concentration below those stipulated in the Appendix IV.

2.3 Highly reactive chemicals, solid chemical wastes, radioactive materials, gaseous materials, asbestos, and spend chemical mixtures that pose an explosion hazard are not covered by this scheme. These are covered in the Labpack Disposal Scheme.

2.4. Standard chemical waste containers are provided by the contractor Enviropace Ltd. If chemical waste is produced, contact Mr Edmond Cheng or Mr H. F.Wong on ext. 6456 to request chemical waste container(s). Enviropace only accepts waste which is collected in their standard containers.

2.5. For low volume waste generators (<4L/month), special arrangements on waste containers will be made.

2.6. Standard waste containers are delivered by HSEO to the waste producer upon request. The following information is required to initiate the delivery: name (students and research assistance should also provide the name of their supervisor), department, waste type, number of containers needed, location of delivery and contact telephone number.

2.7. When the container is three quarters full, complete and submit the "Request for Chemical Waste Collection" form at the HSEO Web Site (http://www.ab.ust.hk/sepo/sub-menu/waste.htm)

2.8. HSEO currently collects and delivers chemical waste containers every Tuesday. If Tuesday is not a working day, the service will be automatically deferred to the next working day.

2.9. To allow sufficient time for preparation of requests to be handled on Tuesday, the requests should be made on Monday before 5:15 pm.

2.10. If a container(s) is(are) to be delivered to an unattended room, please make appointment with Mr H. F. Wong first so that the room will be accessible.

3. Chemical Waste Container and Waste Type

3.1. Enviropace Ltd provides chemical waste containers in 2 sizes, 20 and 200 L. The materials for the containers are plastic, carbon steel, and metal with plastic lining.

3.2. On the body of each 20 L container, there are 2 identical labels showing the waste identity and hazard(s). Users should help to ensure that these 2 labels do not peel off from the container.

3.3. A plastic folder with a chemical waste log sheet inside is attached to the container by HSEO.

3.4. At the present time, Enviropace Ltd provides containers for 13 types of chemical waste. There are containers for spent halogenated solvent, spent non-halogenated solvent, spent inorganic acid, spent alkali, spent lube oil (generators of vacuum pump oil should use traps prior to the pump), spent fixer, spent photographic developer, spent metal solution, spent organic acid, spent hydrofluoric acid, spent cyanide, spent chrome (VI) solution, and gel waste.

4. Chemical Waste Streams

4.1. *Halogenated solvents*: organic solvents with halogens [e.g. chloroform (trichloromethane), trichloroethylene, and dichloromethane)] should be collected in this container and other liquid organic compounds with halogens.

4.2. *Non-halogenated solvents*: this stream is for organic solvents and other organic compounds without halogens (e.g. acetone, hexane, and petroleum ethers).

4.3. *Inorganic acids*: this container is for mineral acids. Organic acids should go to "spent organic acid" container.

4.4 *Alkalis*: sodium hydroxide, potassium hydroxide, and ammonia solution should go to this container.

4.5. *Lube oils*: pump oil, lubricating oil, liquid paraffins, mineral oil and etc. should go to this container.

4.6. *Spent fixers*: This container is for fixing agents used in film and photo processing.

4.7. *Spent developers*: this container is for developing agents used in film and photo processing.

4.8. *Metals solution*: aqueous solutions containing metallic ions or precipitates [expect mercury, chromium(VI) and boron] should be disposed of in this container. Waste containing mercury, chromium(VI) and boron should be collected separately. Enviropace Ltd will provide new streams of waste containers of these metals in the future. For low concentration of these ions (e.g. inorganic mercury>100 mg/L, organic mercury <50 mg/L) in a metal ions solution, segregation can be neglected. Metal ions and precipitates in acid or alkali can also be disposed of in this container. Metallic mercury is not collected in this container. Call HSEO for waste mercury collection.

4.9. *Organic acids*: collect spent organic acids in this container. If the waste generation rate is low (e.g. <4L/month), the organic acids can be disposed of in containers for "spent non-halogenated solvents" or "spent halogenated solvents", respectively, if you have the solvents container already.

4.10. *Hydrofluoric acids*: If a container for this waste stream is not available and the amount of hydrofluoric acid is small, (less than 30% of total volume of inorganic acids waste) the acid can be disposed of in "spent inorganic acids".

4.11. *Spent Cyanides*: The pH of contents within this container must always be kept alkaline to prevent the evolution of a lethal gas - hydrogen cyanide.

4.12. *Chrome (VI) or Boron Solution*: Solutions that contain any chromium(VI) or boron should be placed in the specific container for this (these) waste(s). Enviropace must take specific treatment measures for these two materials and has designated a separate waste stream for them.

4.13. *Gel Waste*: this container is for gel waste such as polyacrylamide and agarose gels, and can include staining materials and/or biological materials in small amounts.

4.14. Waste mixtures will be classified in accordance with the major components in the waste except:

i cyanide: waste containing cyanide should always go to the cyanide waste container.

ii metal solutions containing chromium(VI), mercury and boron: these waste should go to containers designated for these metals. For example, an aqueous solution which contains 1 M each of nickel, silver, and 0.5 M of mercury should be collected in container for mercury waste.

iii If metal solutions or precipitates are generated as waste, they can be put into inorganic acid or alkali containers (if available), depending on the pH. If the pH of the waste is neutral, it should go to “spent alkali”.

iv If the total generation rate of spent fixer and developer is less than 5L/week the spent fixer & developer can both be disposed of to a “spent developers” container.

v Mixtures that contain halogenated chemicals should be put into the “halogenated solvents” container. This special case, and all mixtures which contain halogenated chemicals (even if the halogenated part is the minority component) must be put into the “halogenated solvents” waste container.

4.15. For waste with distinctive liquid phases: the aqueous and organic phases should be separated by decantation and disposed of to appropriate containers respectively.

5. Safety precautions

5.1. Always wear splash proof goggles, gloves and a laboratory coat when handling chemical waste.

5.2. For waste that evolves fumes and vapor, the transferring of waste should be done inside a fume cupboard.

5.3. A new waste should be poured to its corresponding container only after it has passed the compatibility test.

5.4. The compatibility test should only be performed in a fume cupboard.

5.5. To prevent escape of fumes and vapors, close the container tightly each time after the transfer of waste is completed.

5.6. Highly reactive compounds, water reactive compounds, concentrated strong oxidizing or reducing agents should never be mixed with other chemical waste. These chemicals should be bottled separately and will be taken care of under a different scheme. Lists of explosive and water reactive substances are listed in

Appendix V and Appendix VI respectively for reference. Due to the vast number of chemicals available in Hong Kong, these lists should not be considered as exhaustive.

5.7. If chemical waste is handled outside a fume cupboard, the waste handler may need to wear a respirator equipped with the appropriate cartridge. *The operator must be trained in the use of the respirator*. Contact HSEO for information regarding respirator selection and size fitting (ext. 6507). Always wear splash proof goggles, gloves and a laboratory coat when handling chemical waste.

6. Handling of Spent Chemical Mixtures

6.1 Spent chemicals which contain highly reactive compounds, water reactive compounds, concentrated strong oxidizing or reducing agents should never be mixed with other chemical waste. This type of waste should be kept separately in sealed bottles which are made of materials compatible to the waste.

6.2 Perform the compatibility test between the waste ready to pour to the container and waste in the container (refer to Item 7 for the procedures of the compatibility test) before transferring.

6.3 Add new chemical waste into the corresponding container only if it has passed the compatibility test.

6.4 To prevent possible overflow, always check the liquid level in a waste container before new waste is added. The container should only be filled to 70 to 80 % of its full capacity before removal by HSEO.

6.5 Use a funnel and catch tray for spill prevention and control.

Whenever waste is added to a container, immediately enter the information of the new waste to the chemical waste log sheet attached to the container.

7. Compatibility Test Procedures

7.1 This test should be performed inside a fume cupboard by an experienced person.

7.2 Make sure that the air flow of the fume cupboard is “safe” and the sash is lowered to at least shoulder level.

7.3 Draw 50 ml sample from the target waste container into a beaker.

7.4 Insert a thermometer into the beaker.

7.5 *Very slowly* mix in a portion of the new chemical waste that is to be added to the container. The volumetric ratio of the wastes should be similar to that between the original container content and the new waste.

7.6 If bubbling, fuming or a noticeable temperature rise (10 °C or more) occurs during mixing or within 5 minutes, stop the mixing, at once. These signs show that the wastes are incompatible. Store the new waste separately in another container and fill in a new individual chemical waste log sheet.

7.7 If no adverse reaction occurs within 5 minutes, the new waste can be added to the corresponding container.

8. Chemical Waste Log Sheet (see Appendix VI)

8.1. A chemical waste log sheet is essential due to the following reasons:

a. To comply with the chemical waste handling procedures (procedure 4.3) issued by Enviropace Ltd., it states that “every waste entering into a chemical waste container must be properly logged. The filled log sheet must accompany the container at the time of collection by Enviropace. Enviropace will refuse collection of containers that do not carry a legible log sheet."

b. To comply with "Code of Practice on the packing, labeling and storage of chemical wastes" issued by the Environmental Protection Department of Hong Kong.
c. To provide clues for the compatibility of chemical wastes in the container.
d. To provide information for Enviropace Ltd on the treatment of waste.

8.2 In Appendix VI is a sample of the chemical waste log sheet.

8.3 *Fill in all the columns neatly by a pen with dark-colored permanent (water proof) ink.* Pencil, fountain pen, and felt pen with water-based ink are bad examples of writing tools. If labels are not complete or entries are smeared due to use of our incorrect marker, the container will not be collected.

8.4 Write the chemical name of the reagents and wastes (reactants and products of a chemical reaction) in full and in block letters. Abbreviation and short form are not acceptable. Molecular formula of the chemical is helpful. Write down the volume or weight of the waste being poured into the container.

8.5 A log sheet is not necessary for Spent Lube oil, spent fixers and spent developers. A log sheet will not be attached to containers for these waste types.

12.2 Specific Procedures for Neutralization of Some Common Reactive and/or Extremely Toxic Chemicals

As mentioned in 12.1(5.6) above, "Highly reactive compounds, water reactive compounds, concentrated strong oxidizing or reducing agents should never be mixed with other chemical waste." If small quantities of these items require disposal, it is often possible and advisable to neutralize them so that they can be included in one of the standard chemical waste streams listed in 12.1(4). This advisory also applies to small quantities of extremely toxic substances. Specific procedures are given below for safely quenching some common reactive and/or extremely toxic chemicals. If the procedure you need is not listed below, check the following two books in the Safety Library (Rm. 7127): "Destruction of Hazardous Chemicals in the Laboratory" and "Prudent Practices for Disposal of Chemicals from Laboratories".

12.2.1 Acid Halides and Anhydrides

Acid halides, sulfonyl chlorides, and anhydrides are widely used in organic chemistry. The safe disposal of a number of these compounds has been investigated. All of these compounds are corrosive, can cause burns, and some may be lachrymators. In general these compounds react violently with dimethyl sulfoxide (DMSO). A number of other incompatibilities have been noted:
For example

- acetyl chloride reacts violently with ethanol
- propionyl chloride reacts violently with diisopropyl ether
- thionyl chloride reacts violently with a variety of reagents including ammonia, *N,N*- dimethylformamide (DMF), tetrahydrofuran (THF), and ethanol
- sulfuryl chloride is incompatible with lead (IV) oxide, ether, red phosphorus, dinitrogen pentoxide, and alkali
- benzenesulfonyl chloride reacts violently with methylformamide
- acetic anhydride reacts violently with a variety of compounds including boric acid, chromium trioxide, ethanol, nitric acid, and perchloric acid

This list is not exhaustive and standard reference works should be consulted before proceeding. These compounds all react readily, and sometimes violently, with water, alcohols, and amines.

Dimethylcarbamoyl chloride is carcinogenic in experimental animals and sulfuryl chloride may be carcinogenic.

Principle of Destruction

Under controlled conditions these compounds are readily hydrolyzed to the corresponding acids. All operations with these compounds must obviously be carried out in a fume cupboard. Highly reactive compounds (e.g., acetyl chloride, propionyl chloride, dimethylcarbamoyl chloride, benzoyl chloride, thionyl chloride, sulfuryl chloride, methanesulfonyl chloride, and acetic anhydride) are simply added to a 2.5 *M* sodium hydroxide (NaOH) solution at room temperature while compounds of lesser reactivity (e.g., benzenesulfonyl chloride and *p*- toluenesulfonyl chloride) require prolonged stirring or refluxing with a 2.5 *M* NaOH solution. For these compounds destruction was greater than 99.98%. Chlorosulfonic acid is too reactive to be degraded using any of these procedures.

Destruction Procedures

Destruction procedure for highly reactive compounds (e.g., acetyl chloride, propionyl chloride, dimethylcarbamoyl chloride, benzoyl chloride, thionyl chloride, sulfuryl chloride, methanesulfonyl chloride, and acetic anhydride):

Cautiously add 5 mL or 5 g of the compound to 100 mL of a 2.5 *M* NaOH solution. Stir the reaction at room temperature until the reaction is over (it may be useful to monitor the temperature), then neutralize to pH 5-9. When non-toxic byproducts are generated (such as in the case of destruction of acetyl or benzoyl derivatives, thionyl or sulfuryl chloride) the mixture may be poured down the drain. In the case of unknown toxicity, the byproducts should be disposed of in the appropriate organic waste stream..

Destruction procedure for compounds of lesser reactivity (e.g., benzenesulfonyl chloride and p-*toluenesulfonyl chloride)*:

1. Add 5 mL or 5 g of the compound to 100 mL of a 2.5 *M* NaOH solution. Cover and stir the reaction at room temperature for 3 h (benzenesulfonyl chloride) or 24 h (*p*-toluenesulfonyl chloride), analyze for completeness of destruction, neutralize the reaction mixture (to pH 5-9), and discard it.

2. Add 5 mL or 5 g of the compound to 100 mL of a 2.5 *M* NaOH solution. Reflux the reaction mixture for 1 h, cool, analyze for completeness of destruction, neutralize the reaction mixture (to pH 5-9), and discard it as organic waste.

Destruction procedure for compounds of unknown reactivity

To degrade 0.5 mol of the compound, stir a NaOH solution (2.5 *M* , 600 mL) in a 1-L flask and add a few milliliters of the compound. If the compound dissolves and heat is generated, add the rest of the compound at such a rate that the reaction remains under control. If the reaction is slow (e.g., with *p*-toluenesulfonyl chloride), heat the mixture to about 90 °C (e.g., with a steam bath) and, when the compound has dissolved, add the rest of the compound dropwise. When a clear solution is obtained, allow it to cool. Neutralize the final, cooled, reaction mixture to pH 5-9, analyze for completeness of destruction, and discard it in the appropriate waste stream.

12.2.2 Alkali Metals

Principles of Destruction

The alkali metals are allowed to react with an alcohol in slow and controlled fashion to generate the metal alkoxide and hydrogen. The metal alkoxide is subsequently hydrolyzed with water to give the metal hydroxide and alcohol.

Destruction Procedures

Caution! These procedures present a high fire hazard and should be conducted in a properly functioning chemical fume hood well away from flammable solvents. The presence of a nonflammable board or cloth for smothering the reaction, as well as an appropriate fire extinguisher, may be advisable. If possible, do the reaction in batches to minimize the risk.

Sodium and Lithium
Procedures are currently under review (September 2000), and for most recent information you must consult the Departmental Safety Officer.

Irrespective of quantities of sodium or lithium to be destroyed, it is *essential* to ensure that *volatile*, *flammable* solvents are not present.

One of three procedures may be followed, depending upon the situation. Irrespective of which procedure is chosen, *it must be conducted in an area which is away from any organic solvent such that in the event of a fire, containment is assured.*

i. If it is possible to *directly* remove the sodium or lithium from the container (that is, it is present in lumps, or thick strips), add the metal in approx. 1 g lots at a time to 100 mL of *cold* ethanol at such a rate that the reaction does not become violent. Stir the reaction mixture. If the reaction mixture becomes viscous and the rate of reaction slows, add more ethanol. When all the metal has been added stir the reaction mixture until all reaction ceases, then examine *carefully* for the presence of unreacted metal. If none is found, dilute the mixture with an equal volume of water, neutralize, and discard.

ii. If the metal is in the form of wire within, or is unable to be removed easily from, the round-bottom flask, glass bottle or other container, then ensure that no volatile, flammable solvents are present. Sufficient isopropyl alcohol (isopropanol) is then added such as to cover the metal. The reaction should be allowed to proceed until gas evolution is no longer visible. The reaction may be quite slow at the start, and depending upon the quantity of metal present, several hours may be required. An equal volume of anhydrous ethanol is *then* added to ensure that all metal has been consumed. Once gas evolution has ceased, and unreacted metal is no longer present, the mixture is *poured* from the container (*do not add the water to the container*) into a large volume of water (at least equal to three times the total volumes of isopropyl and ethanol used), neutralize, and discard.

iii. If there is residual, *small quantities* (<1 g) sodium or lithium in a *small* volume (< 20 mL) of a volatile, flammable solvent such as hexane or ether in a container such as a beaker, then the best procedure is to allow the solvent to evaporate in the fume hood, and then add the dry metal residue carefully to ethanol, as described above. If residual dry particles of sodium are left in the container, then this can be treated carefully with an excess of cold ethanol. This residue should *not be discarded* until it is verified that *all sodium has been completely quenched*.

Potassium

Potassium is the most treacherous and dangerous of the alkali metals and fires during its destruction are not infrequent. Precautions for its safe handling have been described.

Add the potassium to *tert*-butyl alcohol at a rate so that the reaction does not become violent. If the reaction mixture becomes viscous and the rate of reaction slows, add more *tert*-butyl alcohol. When all the potassium has been added, stir the reaction mixture until all reaction ceases, then examine *carefully* for the presence of unreacted metal. If none is found, dilute the mixture with water, neutralize, and discard it as non-halogenated organic waste. *tert*-Amyl alcohol may also be used. *Whichever alcohol is used it is important to use an anhydrous grade*. If necessary, the alcohol should be dried before use. Powdered 3Å molecular sieve has been recommended for this purpose.

12.2.3 *n*-Butyllithium

Principle of Destruction

Butyllithium is allowed to react with 1-butanol in a dry hydrocarbon solvent to give lithium butoxide and butane. The lithium butoxide is subsequently hydrolyzed to butanol and lithium hydroxide. 1,10-Phenanthroline is used as an indicator. In the presence of excess alkyllithium a red color is produced.

Destruction Procedures

Caution! These reactions should be done under nitrogen and provision should be made for venting, through a bubbler, the considerable amounts of gas that may be generated.

Prepare a 10% (v/v) solution of 1-butanol in isooctane (2,2,4-trimethylpentane) and add 1,10-phenanthroline (1 mg/mL) as an indicator. Dry this solution over a 4Å molecular sieve overnight. Stir 15 mL of the 1-butanol-isooctane mixture under nitrogen in an ice bath and cautiously add 5 mL of a 1.55 M *n*-butyllithium solution in hexanes. After 10 min, or when the reaction appears to have stopped, check the color of the mixture. If it is red, indicating the presence of excess *n*-butyllithium, add more of the 1-butanol-isooctane mixture until a yellow color is produced. When the reaction mixture is yellow add 10 mL of water. Stir the mixture overnight, separate the layers, and discard them appropriately according to waste stream.

12.2.4 Metal Hydrides (except sodium cyanoborohydride)

Destruction Procedures

Lithium Aluminium Hydride

Stir the lithium aluminium hydride under nitrogen in an anhydrous solvent using an ice bath and slowly add 11 mL of ethyl acetate for each gram of lithium aluminium hydride. Ethyl acetate reacts less vigorously than alcohols or water and generates no hydrogen. When the reaction is complete, add a volume of water equal to the initial reaction volume, separate the organic and aqueous layers of the filtrate and discard them according to waste stream.

Sodium Hydride

Note that mineral oil dispersions of sodium hydride (typically 50-60% by weight) are the most commonly sold form of sodium hydride. In this form sodium hydride can be safely handled in air. Pure or 95% sodium hydride (also sold by Aldrich) may inflame spontaneously in air. Thus reactions with or quenching of this form of sodium hydride requires loading it into a flask under an inert atmosphere.

For each gram of sodium hydride dispersion add 25 mL of dry isooctane (2,2,4-trimethylpentane) and stir the mixture under nitrogen with the ability to vent large quantities of hydrogen gas through a bubbler. Then *slowly* add 10 mL of *n*-butyl alcohol (double this amount for pure sodium hydride). Ensure that no unreacted material remains on the side of the flask. After 30 minutes, or when the reaction appears to have stopped, add 25 mL of cold water. Separate the layers and discard them according to waste stream.

Potassium Hydride

Potassium hydride is also normally sold as a mineral oil dispersion, but some fire risk exists when handling this dispersion in air. Handle and dispose as described above for pure or 95% sodium hydride.

Calcium Hydride

Add 1g of calcium hydride to 50 mL of a rapidly stirring ice-water mixture behind a safety shield. Quenching with 95% ethanol is also sometimes recommended in the literature but is found to be extremely slow.

12.2.5 Sodium Cyanoborohydride

As in the case of destruction of simple cyanide salts, the principle here is to oxidize toxic cyanide to non-toxic cyanate.

1. Dissolve each gram of solid sodium cyanoborohydride ($NaBH_3CN$) in 10 mL of water. If necessary, dilute reaction mixtures with water so that the concentration of sodium cyanoborohydride does not exceed 10%. Stir the sodium cyanoborohydride solution and cautiously add 200 mL of a 5.25% sodium hypochlorite solution (available from Park & Shop as "Kao" bleach solution; be sure to use a fresh bottle) for each gram of sodium cyanoborohydride present. Stir the reaction mixture for 3 h. Check that the solution is still oxidizing, and if so, discard it down the drain.

2. For each 80 mL of ether extract that may contain cyanide add 200 mL of a 5.25% sodium hypochlorite solution (available from Park & Shop as "Kao" bleach solution; be sure to use a fresh bottle) and 150 mL of methanol to produce one phase. Stir the reaction mixture for 3 h, check that the solution is still oxidizing, and if so, discard it as non-halogenated organic waste.

3. Pass the exhaust gases through 5.25% sodium hypochlorite solution (available from Park & Shop as "Kao" bleach solution). After standing for several hours check that the solution is still oxidizing, and if so, discard it down the drain.

12.2.6 Sodium Cyanide and other Cyanide Salts

This procedure should only be attempted for small (less than 10 g) quantities of cyanide salts. The principle here is to oxidize toxic cyanide to non-toxic cyanate. In a fume cupboard, dissolve the cyanide salt in water so that the concentration does not exceed 25 mg/mL. For each volume of solution add 1 volume of 1N NaOH and 2 volumes of 5.25% sodium hypochlorite solution (available from Park & Shop as "Kao" bleach solution). Stir for 3 hours and then discard in the appropriate waste stream, or down the drain if no organic co-solvents are involved.

Note: dilution with water is extremely important for cyanide solutions in organic solvents such as dimethyl sulfoxide (DMSO) or *N*,*N*-dimethylformamide (DMF). Exothermic reaction of the organic solvent with sodium hypochlorite solution may result otherwise.

12.3 Procedure for Disposal of Unwanted Chemicals and/or Hazardous Materials: The Labpack Scheme

9. Procedures for "Labpack" Waste Disposal

1. *Introduction*

"Labpack" is another chemical waste disposal service provided by Enviropace Ltd, the chemical waste treatment contractor of Hong Kong Government. It is the packaging, handling, transport and treatment of small containerized waste chemicals.

2. *Waste categories*

2.1 The following items are collected by this scheme:

a. Highly reactive chemicals.
b. Water reactive chemicals.
c. Waste that cannot pass the compatibility test (see Sec. 6 of "Procedures for Disposal of Liquid Chemical Waste at HKUST").
d. Unwanted raw chemicals.
e. Expired chemicals.

2.2 The Labpack service collects chemical wastes in liquid, solid and sludge forms.

2.3 The following items are NOT acceptable by Labpack:

a. Radioactive materials.
b. Explosive materials.
c. Shock sensitive materials.
d. Sealed metal articles or containers
e. Pressurized containers.
f. Any asbestos bearing material and articles contaminated with asbestos.

3. *Handling of Labpack Waste*

3.1. For items 2.1a,b, d and e, keep the chemicals in their original containers as much as possible. If the original container is not in good condition and presents a risk of leakage, wrap and seal the container in a plastic bag or other over pack of compatible nature.

3.2. Fill in and attach a "Labpack waste identity sheet" to each container which contains waste to be collected by the Labpack service. Enviropace does not collect any items without this sheet.

3.3. A sample form of Labpack waste identity sheet may be obtained from HSEO.

3.4. Fill in the identity sheet by a *pen with dark-colored-permanent ink*. Pencil, fountain pen, and felt pen with water-based ink are bad examples of writing tools.

4. *Disposal Procedures*

4.1 Fill in a "Labpack (unwanted/expired chemical) form" for the disposal of unwanted raw chemical, expired chemical.

4.2 Labpack (unwanted/expired chemical) form may be obtained from HSEO.

4.3 Fill in a "Labpack (incompatible waste) form" for waste that:
  a. failed in the compatibility test,
  b. waste mixture contains water reactive and highly reactive chemicals.

4.4 Labpack (incompatible waste) form may be obtained from HSEO.

4.5 Send the completed form by
  a. fax to 2335 1253
  b. internal mail to Environmental Section of HSEO.

4.6 HSEO will send your information to Enviropace Ltd. Since the disposal cost for Labpack waste is very much higher than the liquid waste collected by the 20 L chemical waste containers, each disposal request will be assessed by EPD on individual basis. As a general guideline, waste that can be safely disposed by using the appropriate waste containers listed in section 4 of "Procedures for disposal of general chemical waste" should not be disposed of through the Labpack service.

4.7 After the request is approved by EPD, Enviropace Ltd will collect the waste for disposal.

4.8 All forms are obtainable through your Departmental Safety Officer or his delegate.

As a general guideline, waste that can be disposed of safely through the standard appropriate waste containers listed in Section 4 of "Procedures for Disposal of Liquid Chemical Waste at HKUST" should **not** be disposed of through the Labpack service. For enquiry about the disposal of chemical waste, please contact HSEO Environmental Engineer (ext. 6510), Assistant Health and Safety Officer (ext. 6456) or fax to 2335 1253.

12.4 Procedure for Disposal of Waste Silica Gel/Alumina

At the present time Enviropace does not have a designated waste stream for silica gel or alumina which have been used for purification or chromatographic purposes, and the Labpack scheme is rather expensive. Because finely divided silica and alumina are not acutely toxic (these materials are chronically toxic) HSEO has judged that if properly contained, waste silica gel can be disposed of in the municipal trash. Therefore, waste silica gel or alumina must first be dried. Once dry, should be put in a metal can, plastic bag, or glass bottle. This container must then be enclosed in (another) plastic bag, and then can be disposed of in the normal rubbish.

12.5 Procedure for Disposal of Used Gloves, Tissue Paper *etc.*

Gloves which have been exposed to chemicals should be rinsed with water or detergent and water, wrapped in plastic bags, and disposed into the municipal waste. Tissue paper and towels which have been used in experiments should be dried of residual solvent, wrapped in plastic bags, and disposed into the municipal waste.

12.6 Storage and Labeling of Hazardous Waste Containers

The Chemistry Faculty have agreed that Hazardous Waste Containers may be stored within an approved flammables cabinet, either in the supervisor's laboratory, or in the supervisor's laboratory section of the Central Service Corridor.

In both cases, the containers must be placed in the approved spill trays available from HSEO, and the red label 'CHEMICAL WASTE' must be displayed in the immediate vicinity of the Hazardous Waste Container. The label is obtainable from the Departmental Safety Officer.

Storage of Hazardous Waste Containers in the open Central Service Corridor is not acceptable.

Whenever waste is added to a container, immediately enter the information of the new waste on the chemical waste log sheet attached to the container.

13.0 Emergency Procedures

The procedures below are based on the "HKUST Emergency Procedures" brochure published by HSEO in February 1996. Before presenting these procedures it is important to emphasize that in order to safeguard lives it is necessary to disseminate information regarding the hazards arising from an accident as rapidly and widely as possible. Two important notification principles are:

1. Multiple Parallel Notification

Our laboratory safety engineering controls have been designed so that Security Office are automatically notified if a sprinkler is activated, or if the fire alarm, or emergency ventilation buttons are depressed. However, to provide redundancy in the event that automatic notification for some reason fails, Security Office must always be called (ext 8999) in parallel with activating an alarm. Furthermore, a phone call is the only means of communicating the exact nature and location of the hazard.

Secondly, upon evacuating a room, the *local* alarm system must be activated. If the emergency ventilation button is depressed in the event of a major spill, yellow warning lights will be activated automatically outside the laboratory in question. If there is a fire, in which case the emergency ventilation button *should not* be depressed, the yellow collapsible floor signs marked "Danger-Do Not Enter" may be used. Each laboratory is equipped with two of these signs, and *if it is safe to do so*, one sign should be deployed outside each entrance of the laboratory. Before Security personnel arrive, no-one must be permitted to (re)enter the laboratory.

Finally, the nature of the hazard must be quickly communicated to all those who might be affected by it. Obviously this task can only be performed by those who know what the hazard is. Thus as the occupants evacuate their lab, to the degree it is safe to do so, it is their responsibility to notify all personnel in the neighboring labs.

2. Full Disclosure

One aspect of the "Full Disclosure Principle" has already been mentioned in the discussion above: when notifying persons of an ongoing dangerous condition in your laboratory, it is necessary to tell them in detail the nature of the hazard (i.e. what chemical was spilled or what caused the fire). This principle applies whether you are notifying others during evacuation of your lab, or in the event that people come to your lab to ask what is going on. Even if you judge that the incident is well under control (fire extinguished or spill contained) it is your responsibility to tell them exactly what happened. The answers "nothing happened" or "don't worry, everything is under control" are never acceptable. Full disclosure is not only common courtesy but is also a right of every researcher in the department and every member of the Security and HSEO Emergency Response Teams.

A second aspect of the "Full Disclosure Principle" is that in the event that you successfully extinguish a fire in your laboratory, it is still necessary to call 8999. Security and HSEO will come to the lab to inspect the scene and provide independent assessment that a dangerous situation no longer exists. Fires have been known to reignite, with tragic results.

13.1 Hazardous Materials Spill

The following emergency procedures are intended to provide general guidelines for *spills which involve significant amounts of hazardous chemicals*. These are *general* procedures. Supervisors may need to provide employees and students with further *lab-specific instructions*.

Emergency Response for Chemical Spill

Duties of Constituent Members in the Emergency Response Team (Chemical Spill)

1. Departmental Safety Officer
    - Do not enter the scene, examine the cause and nature of the chemical spill by collecting information from related parties. Evacuate all workers at the scene if necessary.
    - Evacuate all workers immediately for unknown chemical spillage. Further investigate immediately the nature of the spilled chemical(s) with full personal protection equipments including full face-piece respirator, lab coat and chemical resistant gloves, and activate the emergency ventilation system to further investigate the nature of the spilled chemical.
    - Evaluate hazard(s) at the scene.
    - Advise/conduct the clean up procedure with full personal protection equipments, and request HSEO colleagues for assistance if necessary.

2. HSEO
    - evaluate hazard(s) at the scene.
    - advise on clean up procedure, personal protective clothing and emergency response equipment.
    - investigate accident, suggest preventive method(s).
    - provide general assistance as needed.

3. FMO/Security Office
    - incident commander.
    - control of crowd.
    - initiate contact with members of the emergency response team and person in charge of the affected laboratory to start emergency operation.
    - provide general assistance as needed.

3\. FMO/Building Services
- adjust building services equipment to aid in spill control.

Hazardous Material Spill Response Principles

- GET AWAY
- ALERT OTHERS
- GET HELP
- SEAL OFF THE AREA

13.1.1 Hazardous Chemical Spill in a Research Laboratory

The person responsible for causing the spill, as well as the person in charge of the laboratory where spill has occurred, should be present at the scene to provide information about hazardous materials and situation that may be encountered in his/her laboratory. Obviously personnel who have been injured should seek medical attention and not remain at the scene.

Emergency Procedures for Hazardous Chemical Spill in a Research Laboratory

1. Alert your co-workers in the lab. If you are alone, you *must* immediately alert workers in adjacent labs.

2. Press the emergency ventilation system (EVS) button which are present inside labs with fume cupboards and also in the public corridors. The EVS is intended for use in the laboratory if the spill produces toxic or flammable vapors, but is not applicable for biohazardous or radioactive spills, *or if a fire has already occurred.*

3. *If the spill is minor*, irrespective of the hazard nature of the spilled material, ask for assistance and a second opinion. If it is considered *safe* to do so (see 5.2.12 Procedures for Handling the Accidental Release of Hazardous Substances):
   - Confine the spill with appropriate materials.
   - Turn off remotely all heat/ignition sources if flammable vapor is involved.

4. If the spilled chemical produces flammable vapor:
   i turn off all burners.
   ii switch off all electrical equipment which has hot surfaces (for example, hot plate and heating mantle) and/or generates electric spark (for example, brush type motor) NOT in vicinity to the spill.

5. If equipment mentioned in 4ii above is nearby to the spill, interrupt the electricity supply by switching off the main of the bench (sub-distribution board) if the main is away from the spill.

6. Do NOT switch on/off or unplug any electrical equipment nearby to the spill.

7. Evacuate the room. Make sure nobody stays behind, close the door(s) of the laboratory after you leave.

8. Inform the Security Control Centre by dialing 8999. Do not use a telephone nearby to the spill if flammable or toxic vapor(s) are involved.

9. Inform the Security Control Centre of the room number, the name of the chemical and quantity spilled.
   i Provide information on nature of hazard and special aid required if the spilled chemical is very uncommon.
   ii Advise them if anyone has been injured and if medical assistance is required.

10. Keep a safe distance from the laboratory but with the entrance in sight, forbid unauthorized entry to the laboratory and wait for the arrival of the emergency response team.

11. Describe the accident to the emergency response team leader upon his/her arrival.

13.1.2 Hazardous Chemical Spill in a Teaching Laboratory

The person responsible for causing the spill, as well as the person in charge of the laboratory where spill has occurred, should be present at the scene to provide information about hazardous materials and situation that may be encountered in his/her laboratory. Obviously personnel who have been injured should seek medical attention and not remain at the scene.

Emergency Procedures for Hazardous Chemical Spill in a Teaching Laboratory

Students or technicians upon discovering a chemical spill during a laboratory session:

1. Alert all persons in the vicinity immediately.

2. Inform the person-in-charge in the laboratory immediately.

3. If the spill produces toxic or flammable vapors, the staff should press the Emergency Ventilation System (EVS) button of the fume cupboards.

4. Do NOT use the EVS if fire has broken out, or the spill involves biohazardous or radioactive material.

5. If it is completely safe to do so the person-in-charge should:
   i confine the spill.
   ii if the spill produces flammable vapor, instruct students to
   - turn off all burners.
   - switch off all electrical equipment EXCEPT those in immediate vicinity of the spill.

6. If electrical equipment which have hot surfaces (e.g. hot plates, heating mantles), or which generate electric sparks (e.g. brush type motors) is close to the spill, the staff should interrupt the electric supply by switching off the main of the bench (sub-distribution board) if the main is NOT in close proximity to the spill.

7. Do not switch on/off or unplug any electrical equipment nearby the spill.

8. The person-in-charge should evacuate the students and at least one should accompany them to a safe place.

9. The lecturer/TA/ technician(s) should make sure that no persons remain behind, and then close the door(s) of the laboratory after they leave.

10. The lecturer/TA should inform the Security Control Centre by dialing 8999. Do not use a telephone nearby to the spill if flammable or toxic vapor(s) are involved.

11. Provide Security Control Centre (SCC) with information on room number, the name of the chemical and quantity spilled, and whether any injuries have occurred or medical attention needed.

12. As far as possible, the lecturer/TA/technician(s) should keep a safe distance from the laboratory but with the entrance in sight. They should forbid unauthorized entry and wait for the arrival of the emergency response team.

13. The lecturer should describe the accident to the emergency response team (SCC, HSEO) upon its arrival.

13.1.3 Radioactive Material Spill

1. Alert co-workers in the lab.

2. If safe to do so, confine the spill with appropriate materials.

3. Inform the Security Control Centre by dialing 8999.

4. Evacuate everyone in the room. Leave contaminated clothing or articles and close the door.

5. Do *not* activate the emergency ventilation system. In order to prevent others from entering the room, use the yellow collapsible floor sign marked "Danger: Chemical Spill, Keep Away". Each lab has two of these signs. These signs should be deployed as you leave the laboratory, preferably one outside each laboratory entrances.

6. If possible, maintain a safe distance from the scene, keep the entrance(s) or access route(s) in sight and help to prevent unauthorized entry to the laboratory.

7. If conditions allow, remain to assist the emergency response team.

Decontamination Procedures

Persons contaminated by radioactive material should go through decontamination as soon as they arrive at a safe location.

1. Treat any injury first. First-aid workers should protect themselves against contamination.

2. Remove any other suspected contaminated clothing or articles, seal in a plastic bag.

3. Wash contaminated skin area with water and detergent. Avoid aerosol generation (e.g. scrubbing with brush).

4. Immediately seek medical attention for any internal contamination.

13.2 Injury

Be careful

- Note all warning signs
- Learn and use safe work procedures
- Ask questions when in doubt, do not take risk

Be Prepared

- Know the location of emergency shower and eyewash, and make sure they are easily accessible
- Make sure first aid kit is well stocked at all time

- Learn how to use the antidotes if hydrofluoric acid is used
- Learn first aid

When someone is injured...

1. Call the Security Control Centre (SCC) by dialling 8999.

2. Call for Community Emergency Service directly by dialling (9)999 if the situation is urgent or serious and inform SCC subsequently.

3. DO NOT conduct rescue operation unless you know for sure how to perform a proper rescue or you know the situation is safe. A careless rescue operation may endanger the rescuers when, for example, the victim is inside a room filled with toxic gas, or is still in contact with live electricity.

4. DO NOT move an injured person, especially when there are signs of spinal injury or bone fracture, unless it is absolutely necessary to do so for safety reasons.

5. Keep the injured or ill person comfortable, warm, and lying down.

6. Give First Aid treatment if necessary.

   i Acid and alkali burns--flush with running water; use emergency shower if necessary. Do not attempt to neutralize.

   ii Heat or cold burns--flush with cold water.

   iii Chemical in eyes--flush eyes with emergency eyewash.

   iv Major bleeding--apply direct pressure to the wound using a clean cloth.

   v Toxic gas inhalation--expose to fresh air.

   vi Hydrofluoric acid exposure--use antidote immediately

   vii Cyanide exposure—report to clinic or security office for antidote immediately

13.3 Fire

13.3.1 General Precautions

- Do not overload electrical outlets
- Take all necessary precautions when handling flammable substances and heat-generating equipment
- Do not tamper with any fire detection or fire fighting devices
- Do not block fire escape route
- Keep all Fire Doors closed

Be Prepared

- If necessary, develop emergency shut down procedures for processes which may create hazards when unattended.

- Know the escape routes in your work areas.
- Know the location of breakglass fire alarm buttons and fire fighting equipment, and make sure they are easily accessible.
- Know the designated assembly points.
- Learn to use fire fighting equipment.

For more information on Fire Safety, see Chapter 6 of the HKUST Safety and Environmental Protection Manual.

13.3.2 If you hear the fire alarm:

1. Remain calm and check if there is any sign of fire in the vicinity.

2. If you see fire or smoke, or hear the announcement asking you to evacuate, follow the evacuation procedures below.

3. If there is no sign of a fire, stay alert and pay attention to announcements until the fire alarm is silenced.

4. Evacuate if the alarm has sounded for more than two minutes.

5. If you hear the buzzer sound which indicates that the fire alarm is activated in an adjacent fire zone, stay alert and pay attention to any announcements.

6. If you hear both the buzzer and the fire alarm, you are near the boundary of two fire zones. Treat this as if you hear the fire alarm.

13.3.3 If you discover a fire:

1. If safe to do so, try to put out the fire by using fire fighting equipment. Rapid response is critical. If you feel uncertain of your ability to contain the fire, then evacuate the lab, following points 2-6 below.

    i All of the laboratories have carbon dioxide type fire extinguishers (BLACK container). These are good for general purposes, including electrical fire. *Note: these are not suitable for reactive metal or metal hydride fires.*

    ii All synthetic laboratories have dry powder type fire extinguishers (BLUE container). *These should be used for reactive metal or metal hydride fires.*

    iii Sand can be used to contain flammable liquids as well as put out a fire, including reactive metal and metal hydride fires.

    iv A fire blanket can be used when someone's clothing catches fire and can also be placed on a small chemical fire.

    v Water (e.g. from the hose reels) is generally good only for water or paper fires.

    NOTE: If you are successful in extinguishing the fire, you *must* call 8999 to inform Security that a fire occurred and was successfully extinguished. Security and HSEO will come to assess the scene and ensure that no risk of reignition exists. At that time HSEO can then also place an order for a replacement fire extinguisher for your laboratory.

2. Do not take any personal risk. If the fire gets beyond your control, evacuate immediately by following the points 3-6 below.

3. Close the door of the room on fire.

4. Activate the fire alarm by pressing the breakglass fire alarm button.

5. Report to Security Control Centre by dialing 8999.

6. Alert other people to the danger and urge those you see to evacuate. Follow the points in 13.3.5 below.

13.3.4 If your clothing is on fire:

1. *DO NOT RUN.*

2. Drop to the floor and roll your body to extinguish the fire. If the fire blanket is within reach when you discover you are on fire, first pull the blanket around yourself, then drop and roll.

3. If someone else's clothing is on fire, tell them not to panic, and instruct them to drop to the floor and roll. If safe to do so, quickly wrap the fire blanket around them to extinguish the fire.

4. Once the fire is out call 8999 or (9)999 as appropriate to call first aid personnel to the scene.

13.3.5 When there is a fire and you need to evacuate:

1. Remain calm. Walk, do not run, especially when using the staircases.

2. Immediately leave the building and go to the assembly point using the nearest exit.

   Note: the assembly point for Chemistry is the 3/F lawn adjacent to the lab building, facing TV City.

3. Try to help those who may have difficulties travelling such as disabled, injured, and pregnant persons.

4. DO NOT USE THE LIFTS.

5. Report to your Fire & Safety Officer at the assembly point as far as practicable.

6. Do not return to the building until permission is given by the Fire Services Department Officer in charge of the scene.

14.0 Safe Use of Equipment and Apparatus

Whenever equipment or apparatus is to be used, irrespective of its complexity, it is your responsibility to ensure that you understand fully its operation, and all emergency procedures in the event of equipment failure. An equipment malfunction due to improper use amounts to academic misconduct, and will be treated as such. This also applies if there is a fire, flood or other incident arising as a result of improper use of equipment.

14.1 Refrigerators

14.1.1 Refrigerators for Flammable Solvents

All refrigerators and freezers used to store volatile and flammable chemicals MUST be "explosion-proof" as defined by OSHA and NFPA standards. In addition to internal electrical protection, explosion-proof refrigerators offer protection from explosions that may arise from sparking or arcing in electrical components located outside of the refrigerator cabinet. Specifically, the thermostat has been enclosed in a box that has been designed to conform to rigid UL (or equivalent) code requirements. Furthermore, the units have been supplied with a line seal connector ready for final connection in accordance with the local code. Many of these refrigerators are lined with extra steel plating, forming a square steel enclosure.

14.1.2 Storage of Chemicals in Refrigerators

1. Do not store food in refrigerators used for the storage of chemicals. Do not store chemicals in food refrigerators.

2. Always label chemicals to be stored in a laboratory refrigerator with the name of the chemical, the owner, and the date. Use a permanent marker that will not wash off. Chemicals **MUST** be readily identifiable in the event of a power failure or a temperature loss and for later use or disposal.

3. Store chemicals in vapor-tight containers. Do not store chemicals in containers that are uncapped or capped with aluminum foil or foil-lined corks. The best seals for containers are screw tops having conical Teflon or polyethylene inserts.

4. Nitrogen-filled glass ampoules provide the safest method for long-term storage of chemicals.

5. Do not store highly toxic or explosive chemicals in a laboratory refrigerator.

6. Do not store organic chemicals in cold rooms because cold rooms lack appropriate ventilation. Cold rooms should not be used for long-term storage of chemicals. Use a refrigerator.

7. Defrost and clean all refrigerators and freezers at least every 6 months. Identify any unlabeled samples or samples with blurred labels. Dispose of all old or decomposed samples appropriately. It is also recommended to put a label on the refrigerator door indicating the last date cleaned.

8. Do not perform recrystallization by evaporation in refrigerators, as the solvent vapor may corrode the inside of the refrigerator, eventually rendering it unsafe for use. All recrystallizations should be firmly stoppered.

14.2 Sealed Tube Reactions

Small-scale reactions that require moderately elevated pressures are often run in sealed tubes. Although sealed tube reactions are straightforward to carry out, there are difficulties and dangers inherent to any reaction in a fully closed system because of uncontrollable pressure buildup.

Failures of sealed tube reactions are usually caused by

1. Flaws or improper sealing of the tube.
2. Excessive heat or gas evolution.
3. Condensation of oxygen and other gases in the tube during the sealing process.

To run a sealed tube reaction:

1. Estimate the internal pressure buildup expected during the process. The total pressure is the sum of the partial pressures of all the components including:
   a. expanded air (unless under vacuum)
   b. solvent vapor pressure
   c. component vapor pressure (sources of vapor pressure data are given in Appendix 5 of the reference below)
   d. any volume change of reactants or products (e.g., gas evolution). In general, it is not advisable to run a sealed tube reaction in which gas evolution is anticipated.

2. Choose a glass tube of suitable size and wall thickness. Calculated bursting pressures for glass tubing having various wall thicknesses are listed in Table II-1, Appendix 2 of the reference noted at the end of this section. Roughly speaking, 15-20 atm. is the most pressure a small diameter (3/4") heavy-wall tube can withstand; larger diameter tubing will withstand much less.

3. Have the neck of the tube constricted to facilitate sealing. Ensure that the entire tube is annealed and free of strain. A polariscope is available in the glass shop to check for strain.

4. The contents of the tube should be chilled in crushed dry ice and swept with nitrogen and then sealed properly. Chilling the tube in liquid nitrogen is not advised because of condensation of oxygen or inert gases, including nitrogen and argon. Warming a tube containing condensed gases is very likely to cause an explosion. If the tube *must* be sealed using liquid nitrogen as the coolant, it should be done so under pure helium at pressures below one atmosphere.

5. Add the reactants to the tube with a pipette or a syringe, taking care not to leave any chemicals at the point of constriction.

6. The seal on the tube *must* be at least as strong as the rest of the tube and *must* be free of strain. Too thin a seal is weak; too thick is likely to be strained. Seal the tube with a torch, taking care to maintain the original wall thickness at least approximately (note that at this time only the Department glassblowers are authorized to permanently seal vessels with a torch). Anneal the seal immediately in the luminous (yellow) flame to reduce strain. A polariscope is available in the glass shop to check the seal for strain.

7. Allow the tube to come to room temperature behind a shield. Handle it with thick gloves while wearing a face shield.

8. The reaction should be carried out behind a safety shield. A special tube heater with holes for escape of gases provides even heat and will confine flying particles in the event of an explosion. Alternatively, a drilled metal block or a bath of water or sand may be used; if possible, avoid using an oil bath, which may ignite or spatter hot oil if an explosion occurs.

9. Reactions involving very high pressures should be run in specially designed steel vessels. The supervisor and Safety Committee should be consulted for site selection of such reactions.

10. When the reaction is complete, the sealed tube should be allowed to cool to room temperature. Then chill the tube in dry ice before scoring the neck, and open it by touching a hot glass rod to the scored place on the tube. This process should be done behind a safety shield with gloves.

Reference: Shriver, D.F., *The Manipulation of Air-Sensitive Compounds,* McGraw-Hill, New York, 1969.

14.3 Compressed Gases

14.3.1 Hazards of Compressed Gases

If personnel are to use compressed gases routinely in research work, they should take the HSEO course *'Pressure Safety'* (MC 05).

Compressed gases present several hazards:

1. Mechanical failure of the cylinder, cylinder valve, or regulator can result in rapid diffusion of the pressurized contents into the atmosphere, leading to explosion, fire, runaway reactions, or burst reaction vessels.

2. Unsecured cylinders can be knocked over very easily, causing serious injury and damage. Impact can shear the valve from an uncapped cylinder, especially if a regulator is attached, causing a rocketing action or pinwheeling leading to personal injury.

3. Gas cylinders may contain flammable, toxic, or corrosive gases; asphyxiants; or oxidizers.

14.3.2 Storage and Handling of Compressed Gases

1. Check to make sure that a label is attached or that identification of the contents is stencilled on the cylinder when a cylinder is brought to you. Do not accept a cylinder if the contents are not clearly identified. Do not rely on color coding to identify the contents of a gas cylinder; color coding is not standardized.

2. To transport a cylinder, use a hand truck equipped with a chain or belt for securing the cylinder. If a protective cap is available, ensure that it covers the cylinder valve. **Never** move a cylinder while a regulator is attached. Do not

move cylinders by carrying, rolling, sliding or dragging them across the floor. Do not transport oxygen and combustible gases at the same time.

3. Secure gas cylinders to prevent them from falling over. Chains or a clamp-plus-strap assembly are the most common methods of keeping cylinders upright. Make sure the chain is high enough on the cylinder to keep it from tipping over. Cylinder supports are available from the stockroom.

4. Do not store incompatible gases together. Store cylinders of oxygen at least 20 feet away from cylinders of hydrogen or other flammable gases.

5. Store cylinders away from heat (never in areas above 50 °C), including steam or hot water pipes, and away from areas where they might be subjected to mechanical damage.

6. Store full and empty tanks in separate areas. Mark empty tanks when removing them from service to avoid accidental connection of an empty tank to a pressurized system, causing backflow into the tank. When cylinders are delivered they are provided with tear-off labels indicating "Full," "In Service," and "Empty" tanks.

7. Ground cylinders of combustible gases (e.g., to a water pipe) to prevent buildup of static electricity. Keep cylinders away from locations where they might form part of an electrical circuit.

8. Keep the protective cap that comes with a cylinder of gas on the cylinder when it is not in use. The cap prevents the main cylinder valve from being damaged or broken.

9. NFPA codes specify maximum quantities and sizes for hazardous gas cylinders in laboratory areas. A typical laboratory in this department may have no more than three standard cylinders of flammable gases and/or oxygen; two of liquefied flammable gases; and three 4 × 15" cylinders (or volume equivalent) of gases with high Health Hazard Ratings (see NFPA 45).

10. Corrosive or unstable gases should be ordered in the minimum quantities necessary and stored for the shortest possible time (NFPA 45: no more than 6 months). They should be stored in a hood or other safe, dry area. Corrosive gases, if stored for long periods, will corrode the valve internally and may be impossible to open or, if opened, may not close.

11. Gases with Health Hazard Ratings of 3 or 4, or a rating of 2 with no physiological warning properties, **MUST** be kept in an operating hood or other ventilated enclosure. No more than three cylinders with ratings of 3 or 4 may be kept in one enclosure.

12. Cylinders not needed for current use should not be stored in laboratories. Recommended maximum retention periods for gases are 36 months for liquefied flammable gases, flammable gases, and oxygen; 6 months for corrosive or unstable gases or those with a Health Hazard Rating of 3 or 4.

13. When a cylinder is empty (preferably not less than 25 psi residual pressure), close the valve to prevent air and moisture from entering the tank, remove the

regulator (purging it if necessary to safely remove toxic or corrosive gases), replace the cylinder cap, and label the tank "EMPTY". Call OLS to request pickup of the empty cylinder.

14.3.3 Operation of Compressed Gas Systems

The components of a compressed gas cylinder head are visible when the cylinder cap is removed.

The *cylinder valve handwheel* opens and closes the cylinder valve. A few cylinders that do not have handwheels *must* be opened with special wrenches.

The *pressure relief valve* is designed to keep a cylinder from exploding in case of fire or extreme temperature. Cylinders of very toxic gases do not have a pressure relief valve so as to prevent release of the entire volume of gas. It is essential to protect toxic gas cylinders from heat.

The *valve outlet connection* is the joint used to attach the regulator.

The *pressure regulator* is attached to the valve outlet connector to reduce the gas flow to a manageable level. If the regulator does not fit, it may not be suitable for the gas you are using. The Compressed Gas Association (CGA) has intentionally made certain types of regulators incompatible with certain valve outlet connections to avoid accidental mixing of gases that react with each other; some connections even have left-handed threads. Gases should always be used with the appropriate regulator. *The use of adapters is prohibited.*

To operate a cylinder of compressed gas:

1. Make sure that the cylinder is secured before removing the protective cap.

2. Select a regulator with the correct CGA connection for the valve outlet. Use a regulator *only* with the gas for which it is intended. The use of adapters or homemade connectors has caused serious and even fatal accidents. For information on selecting regulators, see the *Matheson Gas Data Book* and/or supplier's catalog. Never open a cylinder without a regulator (not a manual control valve) attached.

3. Inspect the cylinder valve outlet and the regulator inlet for dirt and damage. Install the regulator and tighten the connection with a wrench. Do not force. The cylinder connection is a metal-to-metal pressure seal. Do not use Teflon tape on the threaded parts-Teflon does not prevent leaks and may actually cause the metal seal not to form. *Do not use grease, oil, or solvents on oxygen equipment. Violent explosions can result.*

4. Attach the appropriate hose connections to the flow control valve. Secure any tubing with clamps so that it will not whip when pressure is turned on. Connections should be made with materials that can withstand the pressure and that are chemically compatible with the gas. For example, copper or brass fittings *must not* be used for connections to acetylene because of the potential formation of explosive copper acetylide. Consult the supplier's catalog and MSDS.

5. Install a trap between the regulator and the reaction mixture to avoid backflow into the cylinder. If toxic or corrosive gases are to be emitted from the system, pass the emissions through an appropriate scrubber. When using more than one

gas, install one-way flow valves from each cylinder to prevent accidental mixing and contamination of a cylinder.

6. To prevent a surge of pressure, turn the delivery pressure adjusting screw counterclockwise until it turns freely, and close the flow control valve on the regulator outlet.

7. Slowly open the cylinder valve until the cylinder pressure gauge reads the cylinder pressure. Open the valve fully; limiting flow to the regulator may make it difficult to regulate the delivery pressure. (If the valve will not open, return the cylinder to the supplier. Never tamper with or force a valve. Never use a wrench other than one specifically provided for a cylinder lacking a handwheel). Leak test the cylinder connection.

8. With the flow control valve closed, turn the delivery pressure screw clockwise until the delivery pressure gauge reads the desired pressure. Leak test again.

9. Adjust the gas flow to the system by using the flow control valve or any other flow control device between the regulator and the experiment. If fine control of gas flow is required, a needle valve should be placed downstream of the rough (ON-OFF) flow control valve. Check for leaks throughout the system.

10. After use, close the cylinder valve first, then allow gas to bleed from the regulator. When both gauges read "zero", turn the adjusting screw counterclockwise until it turns freely, and close the outlet needle valve. Remove the regulator and replace the protective cap on the cylinder head.

11. If used with corrosive or flammable gases, the regulator should be flushed with dry nitrogen into a scrubber or the hood. Turn the adjusting screw clockwise, open the outlet valve, and direct nitrogen into the inlet. After flushing, turn the screw counterclockwise and close the outlet valve.

12. Do not allow a cylinder to become completely empty. Leave at least 25 psi of residual gas to avoid contamination of the cylinder by reverse flow. Never attempt to put any gas into a commercial gas cylinder.

14.3.4 Leaking Cylinders

1. A suspected leak in a cylinder of nontoxic or noncorrosive gas can be confirmed by covering the cylinder with soapy water or with special leak detection compound, available from the stockroom. If the cylinder is leaking, try to close the cylinder valve and remove the cylinder to a safe place. Equipment for the specific detection of some gases may be obtained from the gas supplier. If the valve packing is leaking, try closing the valve and tightening the packing nut. Leakage through the valve outlet may be stopped by plugging the outlet with a plug or outlet cap fitted with a gasket.

2. If the leak cannot be stopped, and the gas is flammable or toxic, evacuate the laboratory immediately and notify nearby laboratories, and call Security (ext 8999) to inform them of the nature and location of the problem. If the cylinder is small enough, move it to a fume cupboard if it is judged safe to do so. In the case of a large leak of an asphyxiating gas (such as Nitrogen, Argon, or Helium) evacuation is also necessary. In the case of a slow leak from a cylinder of a

non-toxic and non-flammable gas, call HSEO for assistance. See also Chapter 5.2.12 (E).

14.3.5 Disposal of Some Hazardous Gases

If possible, return the gas in the cylinder to the manufacturer for proper disposal. Call the manufacturer for instructions. Never ship a defective cylinder back to the supplier without permission.

Small quantities of some gases may be bubbled into a solution for destruction—such an operation must be carried out under the direct supervision of the supervisor. Gases such as hydrogen chloride and ammonia are extremely water soluble, and a trap *must* be used to prevent the solution from being sucked back into the cylinder. All the procedures prescribed below are for amounts less than a lecture bottle or sphere size. Do not attempt disposal of larger quantities without approval of the Department Safety Committee.

1. *Flammable Gases: Acetylene, Carbon Monoxide, Hydrocarbons, and Others*

   Remove all ignition sources. Keep the concentration of gas below the explosive range. Remove the tank to a hood, attach a control valve, and allow the gas to dissipate slowly in the hood.

2. *Acid Gases: Hydrogen Chloride, Hydrogen Bromide, Chlorine, Boron Trichloride, Boron Trifluoride, and Others*

   Allow the gas to flow slowly into a solution of about 15% NaOH or other base. Because the reaction is exothermic, do not attempt this procedure if the flow of gas cannot be controlled. Keep the cylinder in the hood until it is emptied. The resulting solution should be neutralized before drain disposal.

3. *Alkaline Gases: Ammonia and Others*

   Remove all ignition sources; anhydrous ammonia is flammable. Bubble the gas through water or a 10%-20% aqueous H_2SO_4 solution. Neutralize the resulting solution before disposal.

4. *Asphyxiants: Nitrogen, Helium*

   Vent in a hood to avoid displacing breathing air from the area.

5. *Sulfur Dioxide*

   Allow the gas to leak into a container of 6M NaOH solution. Add excess calcium hypochlorite [$Ca(OCl)_2$] or commercial bleach solution and let the solution stand for 24 hours.

6. *Hydrogen Sulfide*

   Bubble the gas through a $FeCl_3$ solution. The precipitated iron sulfide may be disposed of as chemical waste in the usual manner.

14.3.6 References

1. Matheson Gas Products, Inc., Guide to Safe Handling of Compressed Gases.

2. Matheson Gas Products, Inc., Matheson Gas Data Book, 6th ed.

3. National Fire Protection Association, NFPA 45, Fire Protection for Laboratories Using Chemicals.

14.4 Glassware

14.4.1 General Procedures

1. Before setting up a reaction, check all glassware for chips and cracks; star cracks in round-bottomed flasks are common and should be repaired in the glassblower's shop.

2. Use a safety shield for reactions run under reduced or elevated pressure.

3. All glassware should be properly clamped, and hosed should be inspected for leaks.

4. If possible, set up equipment over shallow pans to confine spills.

5. Vacuum desiccators and vacuum line bulbs should be wrapped with strong plastic tape or otherwise shielded to help contain flying glass fragments during an implosion.

6. Do not use Erlenmeyer flasks or other thin-walled, flat-bottomed glassware for vacuum work.

7. High-pressure experiments *must* be carried out in areas designed for this purpose.

8. Provide a pressure-relief valve for systems under pressure or connected to a source of high pressure. If necessary, attach a trap to the valve to catch any noxious vapors that may be produced.

9. Adequate hand protection should be used when inserting glass tubing into rubber stoppers or corks or when placing rubber tubing on glass hose connections. *An accident arising by fracture of glass in such an operation represents the most common source of injury in the laboratory*. The following is recommended:
   a. The use of plastic or metal connectors should be considered for connecting plastic or rubber hosing to glass condensers; these are commercially available.
   b. If connectors are not available, robust, protective linen gloves or gauntlets should be worn during any operation involving insertion of glass outlets/tubing/fixtures *etc* into stoppers or plastic/rubber tubing. A towel, or similar device used alone to protect the hands, is *not* recommended.
   c. The plastic/rubber tubing may be fire-polished by the Departmental glassblower, or lubricated at the site of the operation by dipping the end in

acetone, or better, for operations conducted strictly within a fume hood, in chloroform, and applying it immediately to the glass outlet/tubing/fixture *etc*.

d. The glass must be held in a region immediately adjacent to the insertion point to minimize strain on the glass. If it turns out not to be possible to insert the glass tubing with *minimum* effort, the operation should not be attempted.

e. No attempt should be made to remove plastic/rubber tubing from a glass fixture by pulling it away. The excess plastic/rubber tubing beyond the glass fixture should be cut away. A sharp knife or scalpel should then be used to apply parallel cuts along the axis of the remaining plastic on each side to the end of the glass fixture. It should then be possible to peel away the plastic tubing with minimum effort. If the tubing is stuck to the glass, the glass fixture may be immersed in acetone to loosen the tubing.

The Department has purchased several glove types suitable for the foregoing operation. These are available from the DSO.

Glass-blowing operations should not be attempted. In a synthesis laboratory, these both constitute a fire hazard, and for inexperienced operators, represent a common cause of burns. The Department has a fully qualified glassblower.

14.4.2 Precautions to Prevent Flooding

Most laboratory floods are the result of human error or malfunctions in experimental setups that use circulating water. There are several ways to reduce the probability of floods.

1. Check equipment before you leave for the day to make sure that the water is turned off when not necessary. Shut off steam baths before leaving the lab.

2. If you are running overnight experiments, inspect your setups for leaks. Secure effluent hoses of all water-cooled condensers so that they are firmly anchored in the drain.

3. Use hose clamps on tubing connections to reduce the possibility of accidental separation of tubing from condensers and other attachments.

4. Reduce flow to the minimum needed because water pressure increases dramatically at night.

5. Use of special shutoff controls is advised. These devices consist of a flow sensor, which detects an interruption in water flow, and a switch that shuts off both water and electrical power. In addition to preventing floods, this type of flow detector protects equipment and acts as a safeguard against fires and explosions.

14.5 Mechanical Equipment

All mechanical equipment and laboratory instruments should conform to the guidelines for electrical safety (Chapter 14.6). In addition, special mechanical safety features are required for laboratory equipment with moving parts.

Cutting blades. The cutting blades of power tools, tissue slicers, grinders, and paper cutters should be equipped with safety guards.

Vacuum pumps and other mechanical devices. The drive belts of vacuum pumps *must* be protected by a belt guard; unprotected belts can entangle clothing and fingers. All belts, pulleys, drive shafts, chain drives, and rotors should be shielded by guards.

Centrifuges. Securely anchor tabletop centrifuges. Carefully balance samples before centrifuging them. Centrifuges should be equipped with switches that shut off the rotor when the top is opened.

14.6 Electrical Equipment

14.6.1 Procedures

These procedures are largely taken from Winburn' s *Practical Laser Safety.*

1. Assume all electrical circuits are energized until positive action is taken to ensure loss of power.

2. Regard all floors as conductive and grounded unless covered with well-maintained and dry rubber matting of suitable type for electrical work.

3. Whenever possible, use only one hand when working on circuits or control devices.

4. When you must touch electrical equipment (for example, when checking for overheated motors), use the back of the hand. Thus, if accidental shock were to cause muscular contraction, you would not "freeze" to the conductor.

5. Provide overhead runways for extension cords and other plug-in receptacles to keep all electrical leads above floor level and out of walkways.

6. Do not operate electrical equipment if your hands are wet or if you are standing in water. Do not operate electrical equipment where it may come in contact with water.

7. Avoid wearing metallic rings or watchbands when working near high voltages.

8. Turn off all power and pull the plug when repairing electrical equipment.

9. Do not use alligator clips in permanent electrical circuits.

10. Do not use any equipment that you feel may be defective. All repairs of electrical equipment should be made by an electrician or any other qualified individual.

14.6.2 Equipment

1. Laboratory equipment should be fitted with fuses and with three-wire power cords, which provide an independent ground to be the chassis of the apparatus.

2. Outlets for equipment used in fume hoods should be located outside of the hood.

3. Any electric equipment that is operated in the vicinity of volatile and flammable material should have nonsparking induction motors. Refrigerators used to store chemicals should be explosion-proof.

4. Inspect all power cords regularly, and have frayed cords replaced.

5. Extension cords should be used for temporary situations only. Extension cords *must* be heavy-gauge with 3-pronged plugs. The use of lightweight zip cords is prohibited. Extension cords should be no longer than 6 feet and should not be draped over utility fixtures such as lights, water sprinklers, or steam lines. Cords should not clutter the floor in places where they could be stepped on or tripped over. Keep all junctions away from liquids.

6. Some variable autotransformers (Variacs) are not grounded. Make sure that any equipment regulated by such a Variac is independently grounded. Variacs should be fitted with the appropriately sized fuse.

7. High- or low-voltage power supplies should be enclosed to prevent accidental contact and *must* be grounded. The power supply enclosure should have an interlock that disconnects the power and dumps capacitors when the enclosure is opened. Direct-wired equipment should have a readily accessible power disconnect switch. A warning sign should be posted in an appropriate location.

8. Heating elements *must* be enclosed in glass, ceramic, or other temperature-resistant housing. Check the underside of hot plates for any exposed wires.

9. All electrical splices should be secured with a junction box. Use wire nuts and wrap with insulating tape only in a very low-power circuits.

Appendix I

Safety Clearance Form

Safety Clearance Form

This form is to be completed by all non-office personnel in the Department of Chemistry regardless of the length or level of the appointment. This form will be kept in the Office of the Department of Chemistry and will be part of the individual's permanent record.

A note to the students who have finished their UG study in our Department:
If you work in the groups different from those you have done your Chem398 work, you are required to complete this Form again. You can start to work in the new labs only after your new supervisors sign this Form for you.

Appointee Name: ______________________ **Post:** ______________________

Laboratory: ____________ **Lab. Phone No.:** ____________ **Start Date:** ______________

Email address: ________________________ **Supervisor:** ______________________

Department of Chemistry's Safety Policy:

Safety is everyone's responsibility. All activities must be planned carefully to ensure a safe working environment and to comply with the University and statutory regulations. Safety is not the sole responsibility of a single organization or individual—everyone must play their role to ensure a safe working environment.

Occupational Safety and Health (Display Screen Equipment) Regulation

Do you need to use display screen equipment (mainly refers to computers) at work for "prolonged periods of time almost every day"? According to the Code of Practice published under the Regulation, "prolonged periods of time" means: - Operation of display screen equipment continuously for at least 4 hours during a day or cumulatively for at least 6 hours during a day; almost every day, and - Breaks not exceeding 10 minutes in an hour away from the display screen equipment shall not be regarded as breaking the continuity of use of the display screen equipment.	Yes / No (If Yes, please contact Mr. Disney Lau to carry out a risk assessment.) ____________________ Signature of Appointee / Date

Waiver for Theoreticians:

I certify that this appointee will never perform or supervise experimental work and is therefore exempted from completing the Safety Clearance Form, including the "Commitment to understanding of chemical and physical health hazards"	____________________ Signature of Supervisor/Date

"Commitment to understanding of chemical and physical health hazards":

Version 6.0 (03/08)

I, the appointee, do herewith indicate that I shall undertake to obtain all information as is required to appreciate the health hazards posed by the use of all apparatus and all chemicals, including solvents, involved in my work, *prior* to commencing experiments.	Signature of Appointee/Date
I, the supervisor, do herewith certify that I have explained fully to the appointee the details of the foregoing requirement, and where such information may be obtained.	Signature of Supervisor/Date

New Appointees should complete Parts A-C and return the form to Ms. Amy Ho before starting work, or within two weeks of assuming duty, *whichever is sooner*. Faculty need not complete part B or C for themselves, but are reminded of their obligation to take the required safety courses.

New researchers, including PG Students, should return the form after completing Part A, and then complete Parts B-C BEFORE starting Lab work.

Part A. Initial Checklist:
(To be completed by Appointee within two weeks of assuming duty or before starting laboratory work, whichever is sooner)

Item	Description	Appointee sign
1.	I have registered with Ms. Amy Ho for the required HSEO Courses (Chemical Safety in the Laboratory, and Hazardous Waste Management)	
2.	I have received a pair of safety glasses from Mr. Disney Lau (for PG & RA) / Lab supervisor (for UG)	
3.	I wear prescription eyeglasses and have completed the request form for order of Prescription Safety Glasses.	
4.	I have read and understood the following sections of the *Chemistry Department Safety Manual*	
	Chapter 2 "Responsibility for Safety" to Chapter 6.4 "Procedures for Work with Particularly Hazardous Chemicals", and Chapter 14 "Safe Use of Equipment and Apparatus"	
	Chapter 7 "Proper Planning of Laboratory Work" and Chapter 8 "Prior Approval Requirements"	
	Chapter 13: "Emergency Procedures"	

	Laser Users Only: Chapter 9: Laser Safety *and* Chapter 11 of the University *Safety and Environmental Protection Manual*.	

Part B. Basic Lab Safety Orientation
(Conducted by Supervisor prior to the start of lab work)

Item	Description	Appointee sign	Supervisor sign
1.	I have been shown the location of the nearest fire alarm to my lab		
2.	I have been shown the location of the nearest Emergency Ventilation Button and have been instructed under what circumstances it should be used		
3.	I have been shown the location of the nearest Eyewash and Safety Shower		
4.	I have been shown the preferred path for emergency evacuation from the lab and have been shown the location of the designated gathering place		
5.	I have been shown the location of the fire extinguishers, sand pail, fire blanket, and spill kit in my lab, and have been instructed how and when to use these items		
6.	I have been shown the locations of the Emergency Power Shut-off buttons in my laboratory		
7.	**Laser Users only**: I have been shown the location of the Laser Power Supply Shut-off Button, and the Laser Grounding Strip.		

Part C. Need for Additional Required HSEO Safety Courses
(To be completed by Supervisor before the start of labwork and updated as necessary)

Item	Description	(*delete whichever is inappropriate)	Supervisor Sign/Date
1.	I certify that the appointee use lasers in his or her work and take the HSEO "Laser Safety" Course.	will/will not* must/need not*	
2.	I certify that the appointee be exposed to ionizing radiation in his or her work and therefore take the HSEO "Irradiating Apparatus and Sealed Sources" Course.	will/will not* must/need not*	
3.	I certify that the appointee use a respirator in his or her work and therefore take the "Respiratory Training" Course	will/will not* must/need not*	
4.	The appointee must take the following additional HSEO Safety courses:		

Part D. Certification of Receipt of Prescription Safety Glasses and Satisfactory Completion of Required Safety Courses (to be completed by Designated Safety Committee Member within 2 months of start date)

Item	Description	Date	Safety Comm. Initial
1.	Prescription Safety Glasses were received on		
2.	The "Chemical Safety in the Laboratory" course was satisfactorily completed on		
3.	The "Hazardous Waste Management" course was satisfactorily completed on		
4.	Required courses ______________________________, ____________________, ________________________ were satisfactorily completed on		

Appendix II

HKUST Student Safety Clearance at Graduation Form

HKUST Student Safety Clearance at Graduation (Revised March 2008)

Student Name: ________________________ Student ID No.________________

(Surname, Other Names)

Department: _________________ Supervisor: _____________________________

PART I. DEPARTMENTAL SAFETY CLEARANCE

(To be completed by Department)

1. Is departmental safety clearance necessary for this student? (If YES, continue; if NO, sign and submit the form)	Yes / No
2. Did the student clean up	
■ all reagents, unused chemicals?	Y / NA*
■ chemical wastes?	Y / NA
■ experimental setup?	Y / NA
■ any other potentially hazardous setup?	Y / NA
3. Did the student return to the Department	
■ all safety equipment?	Y / NA
■ the Safety Manual?	Y / NA
4. Is the student cleared of any other safety related issues?	Y / N

* NA = Not Applicable

________________________ ________________________

Supervisor Signature Date

________________________ ________________________

Department Head Signature Date

For research postgraduate students, please submit signed form with Report on Thesis Examination Result for Research Degrees (Form-GR6) *to ARR. For other students, please directly send to HSEO for further processing.*

PART II. HSEO SAFETY CLEARANCE

(To be completed by HSEO) Initial & Date

1. Any medical surveillance/user registration record? Y / N ____________
   Admin Section
2. Did the student complete the exit requirement for
   __ Laser worker __ Respirator user __ Radiation worker Y/NA ____________
   __ Animal handler/Biohazard worker
   Admin Section
3. Is the student cleared of any other safety related issues? Y / N ____________
   Field Team

____________________ ____________________

DSEP Signature Date

Appendix III

HKUST Staff Safety Clearance at Termination Form

HKUST Staff Safety Clearance at Termination (Revised March 2008)

Staff Name:______________________________ Staff ID No.________________
(Surname, Other Names)

Dept/Unit:__________ Post:_____________ Supervisor: ___________________

PART I. DEPARTMENTAL SAFETY CLEARANCE

(To be completed by Department)

1. Is departmental safety clearance necessary for this staff? (If YES, continue; if NO, or CONTRACT RENEWED, sign the form and forward to HSEO)	Yes / No / Contract Renewed
2. Did the staff clean up	
■ all reagents, unused chemicals?	Y / NA*
■ chemical wastes?	Y / NA
■ experimental setup?	Y / NA
■ any other potentially hazardous setup?	Y / NA
3. Did the staff return to the Unit	
■ all safety equipment?	Y / NA
■ the Safety Manual?	Y / NA
4. Is the staff cleared of any other safety related issues?	Y / N

* NA = Not Applicable

________________________ ________________________
Supervisor Signature Date

________________________ ________________________
Unit Head Signature Date

Please forward signed form to HSEO for further processing

PART II. HSEO SAFETY CLEARANCE

(To be completed by HSEO) Initial & Date

1. Any medical surveillance/user registration record? Y / N ____________
Admin Section

3. Did the staff complete the exit requirement for
__ Laser worker __ Respirator user __Radiation worker Y/NA ____________
__ Animal handler/Biohazard worker
Admin Section

3. Is the staff cleared of any other safety related issues? Y / N ____________
Field Team

______________________________ ______________________________

DSEP Signature Date

Appendix IV. Safety Self-Quiz Questions

1. Give one example of a chronically toxic material. What steps need to be taken in working with it safely?

2. Name two functional groups implicated to be carcinogenic.

3. What is the proper emergency response for spill of a toxic substance? (give all points, in the proper order)

4. What are the restricted chemicals that require prior approval of the Safety Committee before use?

5. How often must opened bottles of Et_2O or THF be tested for peroxides?

6. What is the definition of a Particularly Hazardous Substance (PHS)?

7. Describe the proper procedure for destroying sodium metal.

8. Explain the danger in performing a very exothermic reaction at too low a temperature.

9. What antidotes are available at the Security Office for use in the event of accidental poisoning?

10. What type of protective eyewear should you wear if you anticipate a significant implosion/explosion risk (for example, when using a new vacuum line for the first time)?

11. Under what conditions must you request a "Pre-Start-Up Inspection" from your supervisor?

Appendix V

SCHEDULE OF SUBSTANCES AND CHEMICALS

Part A	**Code**
Any substance to which the Antibiotics Ordinance (Cap.137) applies	30
Asbestos	09
Dangerous drugs (as defined in the Dangerous Drugs Ordinance (Cap. 134))	10
DG, category 2, NES.. As defined in the	02
DG, category 6, NES.. Dangerous Goods	04
DG, category 9, NES.. Ordinance (Cap.295)	14
Dibenzofurans	19
Dioxins	19
Pesticides (as defined in the Register referred to in Section 4 (b) of the Pesticides Ordinance (Cap.133))	06
Poisons (Part I) (as defined in the Pharmacy and Poisons Ordinance (Cap. 138))	20
Polychlorinated biphenyls	29
Any substance to which the Antibiotics Ordinance [Cap.137] applies	

Part B	
Antimony and its compounds	66
Arsenic compounds	66
Barium compounds	66
Beryllium compounds	66
Boron compounds	66
Cadmium and its compounds	66
Chromium bearing solid tannery waste	56
Chromium and its compounds, NES	66
Cobalt and its compounds	66
Copper compounds/copper etchant	66/76
Cyanides	96
DG, category 3, NES	38
DG, category 4, NES As defined	36
DG, category 5, NES in the	33
DG, category 7, NES Dangerous Goods	35
DG, category 8, NES Ordinance	34
DG, category 10, NES (Cap295)	39
Halogenated organic solvents and compounds	49
Lead and its compounds	66
Manganese and its compounds	66
Mercury and its compounds	66
Mineral oils employed for engine lubrication	73
Mineral oils, NES	63
Nickel and its compounds	66
Non-halogenated organic solvents and compounds	43
Organo lead compounds	86
Organo mercury compounds	86
Organo tin compounds	86
Paints	53
Pesticides (as defined in the Register referred to in Section 4 (a) of the Pesticides Ordinance (Cap 133)	46
Pharmaceutical products and medicines, NES	40
Phosphorus compounds excluding phosphates	68
Selenium compounds	66
Silver compounds	66
Sulphides	98
Thallium and its compounds	66
Tin compounds	66
Vanadium compounds	66
Zinc compounds	66

Acid, alkalis and corrosive compounds	
Acetic acid above 10% by weight	48
Acids or acidic solutions, NES with acidity equivalent to above 5% nitric acid by weight	48
Ammonia solution above 10% by weight	58
Bases or alkaline solutions, NES, with alkalinity equivalent to above 1% sodium hydroxide by weight	58
Chromic acid above 1% by weight	78
Fluoroboric acid above 5% by weight	48
Formic acid above 10% by weight	48
Hydrochloric acid above 5% by weight	48
Hydrofluoric acid above 0.1% by weight	48
Hydrogen peroxide solution above 8% by weight	55
Nitric acid above 5% by weight	48
Perchloric acid above 5% by weight	48
Phosphoric acid above 5% by weight	48
Potassium hydroxide solution above 1% by weight	58
Potassium hypochlorite solution above 5% active chlorine	88
Sodium hydroxide solution above 1% sodium hydroxide by weight	58
Sodium hypochlorite solution above 5% active chlorine	88
Sulphuric acid above 5% by weight	48

NES = Not Elsewhere specified

Appendix VI

The H.K. University Of Science & Technology

Chemical Waste Log Sheet

C.W.P.Reg. No.: 9311-831-T2006-01 HSEO NO.: ______________________
Waste Type: ______________________ CWTF-ID: ______________________
Department: __________ Room No.: ________ Contact Person: ________ Ext. ________

Item	Date	Reagents	Waste Name	Vol. (ml)	User's Name	Extension

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Appendix VII

EXPLOSIVES

Acetyl azide
Acetyl nitrate
Ammonium azide
Ammonium chlorate
Ammonium hexanitrocobaltate
Ammonium nitrate
Ammonium nitrite
Ammonium periodate
Ammonium permanganate
Ammonium picrate
Ammonium tetraperoxychromate
Azidocarbonyl guanidine
Barium azide
Benzene diazonium chloride
Benzotriazole
Benzoyl peroxide
Bismuth nitride
Boron triazide
Bromine azide
Butanetriol trinitrate
t-Butyl hypochlorite
Cadmium azide
Cadmium hexamine chlorate
Cadmium hexamine perchlorate
Cadmium nitrate
Cadmium nitride
Cadmium trihydrazine chlorate
Calcium nitrate
Cesium azide
Chlorine azide
Chlorine dioxide
Chlorine fluoroxide
Chlorine trioxide
Chloroacetylene
Choropicrin
Copper acetylide
Cyanuric triazide
Diazidoethane
Diazodinitrophenol
Diethylene glycol dinitrate
Dipentaerithritol hexanitrate
Dipicryl amine
Disulfur dinitride
Ethyl nitrate
Ethyl nitrite
Fluorine azide
Glycol dinitrate
Glycol monolactate trinitrate
Gold fulminate
Guanyl nitrosaminoguanylidene hydrazine
HMX
Hydrazine azide
Hydrazoic acid
Lead azide
Lead dinitroresorcinate
Lead mononitroresorcinate
Lead styphnate
Mannitol hexanitrate
Mercuric oxycyanide
Mercury fulminate
Nitrocarbonitrate
Nitrocellulose
Nitroglycerin
Nitrosoguanidine
Nitrostarch
Pentaerythritol tetranitrate
Picamide
Picric acid
Polyvinyl nitrate
Potassium dinitrobenzfuroxan
Potassium nitrate
RDX
Silver acetylide
Silver azide
Silver nitride
Silver styphnate
Silver tetrazine
Smokeless powder
Sodium picamate
Tetranitro methane
Tetraselenium tetranitride
Tetrasulfur tetranitride
Tstrazene
Thallium nitride
Trilead dinitride
Trimercury dinitride
trinitrobenzene
Trinitrobenzoic acid
trinitronaphthalene
Trinitroresorcinol
trinitrotoluene
Urea nitrate
Vinyl azide
Zinc peroxide

Appendix VIII

WATER REACTIVE SUBSTANCES

Acetic anhydride
Acetyl bromide
Acetyl chloride
Alkyl aluminum chlorlde
Allyl trichlorosilane
Aluminum aminoborohydride
Aluminum borohydride
Aluminum bromide
Aluminum chloride
Aluminum fluoride
Aluminum hypophosphide
Aluminum phosphide
Aluminum tetrahydroborate
Amyl trichlorosilane
Anisoyl chloride
Antimony tribromide
Antimony trichloride
Antimony trifluoride
Antimony triiodide
Antimony trivinyl
Arsenic tribromide
Arsenic trichloride
Arsenic triiodide
Barium
Barium carbide
Barium oxide
Barium sulfide
Benzene phosphorus dichloride
Benzoyl chloride
Benzyl silane
Benzyl sodium
Beryllium hydride
Beryllium tetrahydroborate
Bismuth pentaflouride
Borane
Boron bromodiiodide
Boron dibromoiodide
Boron phosphide
Boron tribromide
Boron trichloride
Boron triiodide
Bromine monofluoride
Bromine pentafluoride
Bromine trifluoride
Bromo diethylaluminum
n-Butyl lithium
n-butyl trichlorosilane
Cadmium acetylide
Cadmium amide
Calcium
Calcium carbide
Calcium hydride
Calcium oxide
Calcium phosophide
Cesium amide
Cesium hydride
Cesium phosphide
Chlorine dioxide
Chlorine monofluoride
Chlorine pentafluoride
Chlorine trifluoride
Chloroacetyl chloride
Chlorodiisobutyl aluminum
Chlorophenyl isocyanate
Chromyl chloride
Copper acetylide
Cyclohexenyl trichlorosilane
Cyclohexyl trichlorosilane
Decaborane
Diborane
Diethyl aluminum chloride
Diethyl dichlorosilane
Diethyl zinc
Diisopropyl beryllium
Dimethyl dichlorosilane
Dimethylmethane diisocyanate
Disulfury chloride
Dodecyl trichlorosilane
Ethyl dichloroarsine
Ethyl dichlorosilane
Ethyl trichlorosilane
Fluorine
Fluorine monoxide
Fluorosulfonic acid
Gold acetylide
Hexadecyl trichlorosilane
Hexyl trichlorosilane
Hydrobromic acid
lodine monochloride
Lithium
Lithium aluminium hydride
Lithium amide
Lithium ferrosilicon
Lithium hydride

WATER REACTIVE SUBSTANCES (Cont'd)

Lithium peroxide
Methyl aluminum sesquibromide
Methyl dichlorosilane
Methyl isocyanate
Methyl magnesium bromide
Methyl magnesium iodide
Nonyl trichlorosilane
Octyl trichlorosilane
Phosphonium iodide
Phosphorus oxychloride
Phosphorus trisulfide
Phosphorus oxybromide
Phosphorus pentachloride
Phosphorus tribromide
Polyphenyl polymethyl isocyanate
Potassium hydride
Potassium peroxide
Pyrosulfuryl chloride
Silver acetylide
Sodium aluminum hydride
Sodium hydride
Sodium oxide
Sodium-potassium alloy
Sulfonyl fluoride
Sulfur chloride
Sulfur trioxide
Thiocarbonyl chloride
Thiophosphoryl chloride
Toluene diisocyanate
Triethyl aluminum
Trimethyl aluminum
Tri-n-butyl borane
Trichloroborane
Triethyl stibine
Trimethyl stibine
Trisilyl arsine
Vanadium trichloride
Zinc acetylide
Zinc peroxide
Lithium silicon
Methyl aluminum sesquichloride
Methylene diisocyanate
Methyl trichlorosilane
Methyl magnesium chloride
Nickel antimonide
Octadecyl trichlorosilane
Phenyl trichlorosilane
Phosphoric anhydride
Phosphorus pentasulfide
Phosphorus (amorphous red)
Phosphorus sesquisulfide
Phosphorus trichloride
Potassium
Potassium oxide
Propyl trichloride
Silicon tetrachloride
Sodium
Sodium amide
Sodium methylate
Sodium peroxide
Stannic chloride
Sulfuric acid (>70%)
Sulfur pentafluoride
Sulfuryl chloride
Thionyl chloride
Titanium tetrachloride
Trichlorosilane
Triisobutyl aluminum
Tri-n-butyl aluminum
Trioctyl aluminum
Triethyl arsine
Trimethyl arsine
Tripropyl stibine
Trivinyl stibine
Vinyl trichlorosilane
Zinc phosphide

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