Marquette University
Chemistry Department

CHEMICAL HYGIENE PLAN
AND
SAFETY MANUAL

Emergency Telephone Numbers

Public Safety	X6800
Fire, Police, Ambulance	1911
Poison Control Center	266-2222

Preface

The purpose of this document is to furnish Marquette University Chemistry Department students, faculty and staff with safety guidelines. These guidelines apply to both the teaching and research laboratories.

Safety Committee
August 9, 2001

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Marquette University
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NOTE: Insert CARBON form between sheets before filling out this Report.

ACCIDENTAL INJURY REPORT

Time and Place of Accident____

NAME of Injured Person____

Was Injured person a Student? Yes_____ No_____ Course #_______ Lab Section______Room_________

NAME and Category of Supervisor____
(Teaching Assistant, Faculty, etc.)

DESCRIBE Accident (include the injured's activity, equipment and/or chemicals used and part of the body injured and by what)

____
____
____
____
____

Nature and Extent of Injury____
____

Type of First-Aid, by____

Student Health Center? Yes__________ No___________

Hospital Treatment? Yes__________ No__________ Name of Hospital___________________________

Principal Cause(s) of Accident and Injury____
____
____
____

Aggravating Causes____
____
____

What should be done and by whom to prevent a recurrence of this or similar accidents?

____
____
____
____

Signature of Injured Person____________________________________ Date___________________

Report Filed by____ Date_____________________

Please give this Report to the Lab Coordinator.

Marquette University
Department of Chemistry
August 14, 2001

TO: Chemistry Faculty and Teaching Assistants

SUBJECT: Eye Protection

Safety in the laboratory is one of the most important aspects in the training of any individual. Among the safety practices, prevention of injury to the eyes is of perhaps the greatest importance, both because of the probability of such injuries and because of the tragic consequences in the case of a permanent injury. Yet, in most cases, such injuries could have been prevented simply by wearing protective equipment.

We shall continue the following practices:

1) All Teaching Assistants are instructed and authorized to dismiss any student now wearing safety goggles or other suitable protective equipment from the laboratory. (If a student forgot his/her personal safety goggles, he/she should go to the stockroom to borrow an emergency pair of use on that day.)
2) All Teaching Assistants are instructed to report to the Departmental Office any student who causes him/her any problems in enforcing this rule. An example might be a student who repeatedly removes his/her goggles in the laboratory.
3) All instructional staff without exception are expected to enforce the above practices.

Charles Wilkie
Chair & Professor

Acknowledgement by Teaching Assistants:

I have received a copy of this notice and understand it. I also understand that a similar notice [1) and 2) above] will be posted in the undergraduate laboratory where I am the laboratory instructor.

____

Chemical Hygiene Clearance

I have read and understood the contents of the Chemical Hygiene Plan and Safety Manual and I am familiar with the hazards associated with the chemicals in use in my work area.

I,____________________, have discussed chemical hygiene procedures with,
faculty member
____________________, and he/she is familiar with the hazards associated with
student
the chemicals in use in our laboratory.

____________________________ __________________
student date

____________________________ __________________
faculty member date

Chemical Hygiene Plan

Part I – Introduction

Policy

Within this manual, the Chemistry Department at Marquette University delineates the means for providing a safe and healthy workplace in compliance with the Occupational Safety and Health act of 1970 including CFR 1910.1450 "Occupational Exposure to Hazardous Chemicals in Laboratories", the "Laboratory Standard".

Objective

This document establishes the Chemical Hygiene Plan and Safety Manual for the Chemistry Department. Our objective is to describe correct practices, procedures, operations equipment and facilities to be followed by faculty, students, employees, visitors and any personnel working in a laboratory or stockroom of the Department to protect them from potential health hazards presented by chemicals used in these areas and to maintain exposures below safe, specified limits. It is the full responsibility of the faculty, research and supervisory personnel to know and to follow provisions of this Plan.

Personnel Covered by the Plan

This Plan and Safety Manual applies to all work involving hazardous substances conducted in space assigned to the Chemistry Department in the Todd Wehr Chemistry Building and in Todd Wehr Physics 007.

Disclaimer

The materials contained in the manual have been compiled to provide a basic safety manual for use in the Marquette University Todd Wehr Chemistry Building. It is intended to serve as a starting point for good practices and does not purport to specify minimum legal standards. No one should assume that all necessary warning and precautionary measures are contained in the document or that other or additional information on measures may not be required.

Acknowledgement

Many portions of this document were drawn from the ACS pamphlet "Safety in Academic Chemistry Laboratories", the text "Prudent Practices for Handling Hazardous Chemicals in Laboratories", the MIT "Chemical Hygiene Plan and Safety Manual" and the Dartmouth College "Chemical Hygiene Plan and Safety Manual".

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Part II – Responsibility, Authority

Department Chairperson

This person has the responsibility and authority to insure that the Plan and Manual is written, updated and implemented. The Department Chairperson appoints a Chemical Hygiene and Safety Committee, as well as a Chemical Hygiene Officer. The Department Chairperson has responsibility for the health and safety of faculty, students, employees, visitors and other personnel conducting work in the assigned laboratories of the Department.

Chemical Hygiene and Safety Committee

This committee assists the Chairperson with implementation and updating of the Plan and Manual as well as providing advice to faculty members (principal investigator and supervisor) with respect to training and implementation. This committee is chaired by the Department's Chemical Hygiene Officer. Current members of the Chemistry Department Chemical Hygiene Committee follow:

Dr. Jayaraman, Chair	Mr. Ausman
Dr. Rathore	Mr. Konkol
Dr. Lukaszewski-Rose	Mrs. Nowak

Laboratory Supervisors

The Supervisor's duties as defined in the Plan are the responsibility of the principal investigator (faculty member) in charge of each laboratory. In addition, supervisors of the undergraduate laboratories have comparable responsibilities.

The primary responsibility of the faculty member is to implement the Plan and ensure compliance with the OSHA Lab. Standard. The faculty member duties include, among other, the following:

- Instruct all personnel to conduct work in accordance with the Department's Chemical Hygiene Plan;
- Define the location of designated areas for work with particularly hazardous substances and ensure that an inventory of these substances is properly maintained;
- Review and approve standard operating procedures for work involving hazardous substances;
- Define hazardous operations, designating safe practices and specifying protective equipment;

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- Ensure that all staff receive instructions and training in safe work practices, use of personal protective equipment and procedures for dealing with accidents involving toxic substances;

- Direct all personnel to obtain protective equipment necessary for the safe performance of their job;

- Monitor the safety performance of personnel with regard to required safety practices and techniques;

- Conduct formal laboratory inspections regularly to monitor compliance with existing laboratory procedures and regulation;

- Formulate procedures for dealing with accidents that may result in the unexpected exposure of personnel or the environment to toxic substances;

- Investigate all accidents and report them to the Chemical Hygiene Officer. Institute procedures that will minimize the repetition of accidents;

- Report to the Chemical Hygiene Officer incidents that cause (1) personnel to be seriously exposed to hazardous chemicals or materials, or that (2) constitute a danger of environmental contamination;

- Take action to correct work practices and conditions that may result in the release of toxic chemicals;

- Instruct laboratory personnel to properly dispose of unwanted and/or hazardous chemicals and materials;

- Make copies of the approved Chemical Hygiene Plan and Safety Manual available to the support staff;

- Arrange for non-laboratory personnel (e.g. contractors and support personnel) to be informed of potential hazards they may be exposed to when working in the laboratory and provide proper instruction to minimize the risk of harmful exposure to hazardous substances;

- Ensure that an updated inventory list of particularly hazardous chemicals (e.g. peroxidizable and explosive types, short lived chemicals, etc.) is maintained. Such chemicals should be labeled with date received and a decision date for disposal.

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Employees, Staff and Research Personnel

Employees, as defined by the Plan, are those staff personnel under the direction of the faculty member. Employees not under the direction of the faculty member, but who are in an area under the direction of the faculty member, are also subject to the Plan and the standard operating procedures in effect in that area. Also subject to the Plan are all "non-employee" personnel including graduate and undergraduate students, postdoctoral associates and visiting scientists.

It is the responsibility of employees and other non-employee personnel to follow the procedures outlined in the Plan and all standard operating procedures developed under that Plan. These include the following:

1. Understand and follow all standard operating procedures;

2. Understand all training received;

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

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

5. Report to your supervisor and the Chemical hygiene Officer all facts pertaining to every accident that results in exposure to toxic chemicals and any action or condition that may exist that could result in an accident. Report accidents by filling out the appropriate standard accident forms and forward same to your supervisor or responsible faculty member.

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Part III - Information and Training

Initial Training

All personnel in the Department of Chemistry must complete the following steps prior to working in areas where hazardous chemicals are in use.

- Read and understand the Department's Chemical Hygiene Plan and Safety Manual; submit a signed and dated copy of the Chemical Hygiene clearance to the Chemical Hygiene Officer viz. "I have read and understood the contents of the Chemical Hygiene Plan and Safety Manual and I am familiar with the hazards associated with the chemicals in use in my work area". The section of the clearance form, which reads "I have discussed chemical hygiene procedures with __________ and he/she is familiar with the hazards associated with the chemicals in use in our laboratory" must be signed by the faculty member.

All personnel whose work will involve the use of hazardous substances must attend the Chemical Hygiene Lecture or videotape of this lecture each January. Other personnel starting work after January must also view this videotape prior to laboratory operations. A record of personnel who have attended or viewed the videotape of the lecture will be maintained by the department.

Undergraduate students enrolled in laboratory coursed must read and understand and sign a clearance form, which covers safety aspects in general chemistry and organic chemistry, etc. courses (see Appendix for these forms). Teaching assistants are required to attend special safety training sessions prior to assuming assigned duties; these are offered by the Chemical Hygiene Officer or his/her appointee.

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Material Safety Data Sheets (MSDS's)

Material Safety Data Sheets (MSDS's) are valuable sources of information on hazardous substances. All personnel who may be exposed to hazardous substances may request a copy of the "Right to Know Pocket Guide for Laboratory Employees". (Genium Publication Corp. 1990). This is an excellent guide to understanding MSDS's as well as delineating safety tips, physical and health hazards, chemical exposure limits, terms and abbreviations on labels and in MSDS's.
MSDSs should be the first source of information about the hazards associated with a chemical.
Typically, MSDSs will contain the following information, usually in separate sections on the sheet:

- name, address, and phone number of manufacturer
- chemical name, synonyms, and Chemical Abstracts (CAS) Number
- physical properties
- a listing of hazardous constituents for mixtures
- health hazard information
- first-aid measures
- fire fighting measures
- handling and storage precautions
- exposure controls/personal protection
- stability and reactivity

Newer MSDSs will contain the following additional information:

- toxicological information
- ecological information
- disposal considerations
- transport information
- regulatory information
- other information

Manufacturers are required to provide a MSDS for each chemical product sold. The second floor stock room can provide you with the MSDS for the chemicals you are using.

In addition a number of companies such as Aldrich provide MSDS at their web site. Other web sites with connections to MSDS data sheets
http://physchem.ox.ac.uk/MSDS/#MSDS
http://www.ilpi.com/msds/index.html#Internet
http://hazard.com/msds/index.php

Other Sources of Information

For any additional information chemical safety references and books are available in the second floor stock room.

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Part IV - Safety in the Teaching Laboratories

At the beginning of the academic year, a meeting will be held for all teaching assistants and laboratory coordinators. The purpose of the meeting will be to orient the laboratory teaching staff in safety practices in the undergraduate laboratories.

A. The teaching staff should become familiar with the location and use of safety facilities and supplies.

   1. Safety showers and eye washes are located in the laboratories and in the corridors. Instructors should tell their students to remember the location of the nearest shower and eye wash to their working areas.
   2. Fire extinguishers are to be used in case of a fire. Breaking the seal on the extinguisher indicates that it has been used. The stockroom should be notified that a repressurizing is needed.
   3. First aid kits are found in the stockrooms. They should be used without hesitation when an accident occurs.

B. Common sense measures should be followed in the laboratories. For example, acids and bases should be washed off the skin as soon as possible after contact; flammable solvents should never be heated in the open over a flame; reactive chemicals should be mixed slowly with caution, etc. For the safety of the cleaning crew combustibles like paper should be placed in the tall waste containers at the end of the benches; chemicals and noncombustibles like broken glass should be placed in the short waste containers along the wall near the hoods.

C. If an accident occurs, the "Accidental Injury Report" should be obtained from the stockroom immediately and should be completed immediately in duplicate and turned into the Laboratory Coordinator, TW205, or Department Office, TW101. A copy of the report is given in Appendix 1.

D. The procedure for obtaining medical treatment for accidents in undergraduate laboratories is as follows:

   If a minor injury has occurred, the Public Safety Department should be called from the stockroom telephone. The emergency number is 1911. the accident should be described briefly and a request made to take the injured student to the Student Health Service. Give your location. The Health Service is open from 8:30 a.m. to 4:30 p.m. If injury occurs at some other time, treat it as you would a major injury (see below).

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If a major injury has occurred, the Public Safety Department should be called as in the case of a minor injury. The accident should be described briefly and a request should be made to take the student to the emergency room of a hospital. The Public Safety officer will usually take the injured person to Mt. Sinai or Good Samaritan Hospital.

E. Safety goggles must be worn by students and instructors at all times in the undergraduate laboratories. Instructors are expected to dismiss from the laboratory any student not wearing safety goggles or other required safety equipment. Students who cause instructors trouble in enforcing the goggles requirement should be reported to the Laboratory Coordinator. At the beginning of each semester, instructors will announce the compulsory goggles requirement to the students in their sections. The requirement will be posted in each laboratory also.

At the meeting referred to earlier at which teaching assistants and laboratory coordinators are oriented to safety practices, a memorandum on the goggles requirement will be distributed. Teaching assistants will be required to sign a copy acknowledging receipt and understanding of the department's rules on goggles in the laboratory. A copy of the memorandum is given in Appendix 2 and Attachment 2.

F. An occasional occurrence in the laboratory is the breaking of thermometers with consequent spilling of mercury. The spillage can be picked up as an amalgam. A powder made for this purpose is available from the second floor storeroom. The powder should be used immediately after mercury spillage.

Non-biodegradable chemicals should not be poured into the laboratory sinks. Instead, a bottle will be provided for the students to discard these chemicals. The bottle should be labeled with the name of the chemical and given to the stockroom after it is no longer in use.

G. Laboratory instructors should familiarize themselves with the chemicals being used in an experiment (e.g. corrosiveness, flammability, reactivity, stability and toxicity).

H. Students should be encouraged to wear appropriate clothing including a protective apron or laboratory coat. Long hair should be confined. Open-toed shoes or sandals should be discouraged.

I. Eating, drinking and smoking are not allowed in the laboratories.

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Part V - Medical Consultation and Emergency Procedures
Emergencies and Accidents

In case of an injury or accident, it is prudent practice to call Public Safety. 1911 is used in case of emergencies and 86800 is used for non-emergencies.

For a minor injury, students can request help by going to the Student Health Service. For major injuries, minor injuries of non-students or when the Health Service is closed, you should request help in going to the Emergency Room of a hospital. The Public Safety officer will usually take the injured person to Mt. Sinai or Good Samaritan Hospital.

Fire

In the even that a fire is uncontrollable, in that it cannot be extinguished by a fire extinguisher, a fire alarm should be sounded. Fire alarms are located near the stairways on all floors. They are activated by lifting. Faculty, students and staff should familiarize themselves with the alarm locations near their offices and laboratories.

Activating the fire alarm will set off a pulsing ringing on all floors of the Todd Wehr Chemistry Building. When the fire alarm sounds, the building should be evacuated immediately. <u>Stairs should be used; the elevator should not be used.</u>

Accidents Involving Chemicals

In the event of a toxic spill, follow procedures described in this document. Obtain help from 2nd floor storeroom, consult the appropriate MSDS and clean-up promptly.

Every laboratory door is posted with an information card with the names and phone numbers of personnel to be called in the event of an emergency.

Accident Reports

Accident reports should be filled out describing the nature of all accidents as well as action taken to avoid such accidents in the future. Copies should be sent to the Chemical Hygiene Officer and to the supervisor or faculty member. A spill of a hazardous/toxic substance that occurs outside a designated and confined area also mandates a written report.

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Part VI - Protective Equipment

Eye Protection

Department policy requires that all personnel, including visitors, wear eye protection (either safety glasses, safety shields or safety goggles) at all times when in the laboratories. Ordinary prescription glasses are not adequate protection against injury from flying particles, etc. Use is limited to providing minimal protection when present in the laboratory where an experiment is not being conducted.

Either full face shields or safety shields should be used when handling potentially hazardous (explosive compounds).

Laser or ultraviolet light operations require the use of special glasses or goggles.

Protective Apparel

Suitable gloves must be worn when handling hazardous/corrosive chemicals. Gloves should be inspected carefully to insure that they are free of holes and tears.
Skin contact with any chemical (obvious exceptions, water, salt, etc.) should be avoided.

Wearing of laboratory coats or aprons on a regular basis in the laboratory is a sensible way to prevent injury.

Sandals or open toes shoes should not be worn in the laboratory. Legs require protection, thus shorts or short skirts are inappropriate in the laboratory. Long hair or lose clothing should be confined when in the laboratory.

Laboratory Hoods

Fume hoods must be used when conducting laboratory experiments with hazardous chemicals. Fume hoods of all sizes are available in the research and instructional laboratories. Obstructions caused by large objects, reagent bottles, etc., can cause turbulence/abnormal air flow patterns, which result in inefficient and dangerous hood operations.

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Average face velocity for the 6' and 8' hoods located in the research and advanced chemistry laboratories is 100'/minute. If a given 18" sash opening results in a velocity of <100'/minute, then a lower sash height (causing an increase to 100') is labeled with a marker, which indicates the maximum safe operating sash height. Safety factors that should be kept in mind when operating within a hood are outlined in "Prudent Practices for Handling Hazardous Chemicals in Laboratories" pp. 199-200. Among these are:

- The hood sash should be maintained in the lowest possible position; this will not only provide optimum fume containment, but the lowered sash may also act, in part, as a safety shield. Keep the sash closed when the hood is not used.

- Keep the hood clean without bottle or equipment clutter. Hoods should not be used for storage of chemicals.

- An emergency plan should be devised in the event of ventilation (power) failure or other unexpected events (fire/explosion) in the hood.

Fire Extinguishers, Safety Showers, Eyewash Facilities and First Aid

Laboratories are equipped with CO_2 extinguishers as well as several other types. Each laboratory must contain at least one fire extinguisher. The seals should not be broken on the release handle. If the seal is broken, then the fire extinguisher needs immediate repressurizing. The stockroom should be notified of the need.

- CO_2 extinguishers for Class B (flammable solvents) and Class C fires (electrical. Do not use them in fires involving reactive metals (Na, K, Al, lithium aluminum hydride, etc.).

- Dry Powder extinguishers for Class B & C fires.

- Met-L-X extinguishers for burning reactive metals, metal alloys, hydrides, organometallic compounds (Class D).

- Sand for any type of fire, especially Class D.

- Water extinguishers for Class A fires (wood/paper/trash) only.

Research personnel are instructed annually by the Safety Committee on the proper use of these extinguishers. Instruction includes hands-on demonstrations.

The Chemical Hygiene Safety Committee will conduct unannounced laboratory inspections several times each year. These are thorough inspections, which include surveys of safety equipment, fire extinguishers, laboratory housekeeping, hood conditions, chemical and solvent storage, etc.

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Part VII - Standard Operating Procedures for Work with Hazardous Substances

The OSHA Laboratory Standard (29CFR 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 which act on the hematopoietic systems and agents which damage the lungs, skin, eyes or mucous membranes". Highly flammable and explosive substances obviously comprise an addition category of hazardous chemicals.

Carcinogens

In order to familiarize personnel with the classes of compounds and functional groups that have been correlated with carcinogenic activity, a listing of these types is given in Appendix 4. The select carcinogens are asterisked. These compounds are particularly hazardous and there is evidence from human studies that exposure to such chemicals can cause cancer. The listing that follows were drawn from substances identified as carcinogens or potential carcinogens by OSHA, the International Agency for Research on Cancer and publications by the National Toxicology Program.

Reproductive Toxins

These compounds cause chromosomal damage (mutagens) and have lethal or teratogenic effects on fetuses. Many toxins exhibit chronic effects causing damage as a result of lengthy exposures with symptoms, which become evident only after long latency periods. The following Table lists some common chemicals suspected to be reproductive toxins.

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

This listing is not complete. Researchers and their supervisors should evaluate compounds used in their work that have similar structures and determine if they should be handled as reproductive toxins. The periods of greatest susceptibility to embryo toxins is the first 17-55 days of pregnancy. Women of child bearing potential should avoid all skin contact with such chemicals, even if they are not sure that they are pregnant. Reassignment to other duties may be in order in such cases.

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Corrosive Substances

These materials cause destruction or visible alterations in living tissue at the site of contact. Corrosive chemicals include strong acids, strong and some weak (ammonium hydroxide) bases, dehydrating agents (sulfuric acid, sodium hydroxide phosphorous pentoxide, calcium oxide) and oxidizing agents such as hydrogen peroxide, chlorine, bromine.

Irritants

These substances are non-corrosive, but cause reversible inflammatory effects on tissue at the contact side. A very large number of both organic and inorganic chemicals fall into this class and therefore skin contact with almost all chemicals should be avoided.

Toxic and Highly Toxic Agents

OSHA regulations define toxic and highly toxic agents with median lethal dose (LD_{50}) values in the following ranges:

	Toxic	**Highly Toxic**
Oral LD_{50} (albino rates)	50-500mg/kg	<50mg/kg
Skin Contact LD_{50}	200-1000mg/kg	<200mg/kg
Inhalation LD_{50}	200-2000 ppm/air	<200 ppm/air

Hazardous Substances with Toxic Effects on Specific Organs

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

Sensitizers

A sensitizer or allergen is a substance that causes allergic reaction in normal tissue after repeated exposure to the substance. Examples of allergens include diazomethane, chromium, nickel, formaldehyde, isocyanates, arylhydrazines, benylic and allylic halides, and many phenol derivatives.

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Flammable and Explosive Substances

A number of highly flammable substances are in common use in the 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. Examples include acetylene, hydrogen, carbon monoxide and hydrogen sulfide. Acetylene and hydrogen are especially dangerous because of their wide flammability limits, which in turn add greatly to their potential fire and explosion hazards.

Procedures for Laboratory Work with Hazardous and Toxic Substances

It is not within the framework of this document to provide standard operating procedures for specific hazardous substances. Too little is known about many of the thousands of compounds that might be involved in research operations. Instead, in the following section, general procedures are suggested for work with any and all hazardous substances. Recently, every issue of the Chemical and Engineering News has a brief section on chemical safety. The section is found at the beginning of the "Letters" section. Researchers should read these weekly safety communications.

A Partial List of Good Laboratory Practices

- All work areas should be maintained in a clean and orderly manner.
- Reagent, solvent clutter on floors and in hoods must be eliminated. Also exit obstructions must be eliminated.
- Researchers should make an effort to label all materials used and be aware of their flammability, reactivity, corrosiveness and toxicity.
- All laboratory set-ups should be reviewed for safety by the researchers and coworkers.
- All accidents that require medical attention must be reported and reviewed by the safety committee.
- Compressed gases must always be secured to avoid being knocked over. Large tanks require belt clamps or chains. Small tanks require a base of a large diameter that clamps on the tank. The clamps and bases can be ordered from the stockroom.
- Vacuum pumps should have belt guards. The guards prevent clothing or part of the body form being caught in the pump's moving parts.
- Most refrigerators and freezers in the Todd Wehr Chemistry Building are designed to store flammable materials. There are a few that are not. These should be clearly marked. Signs may be obtained from the stockroom. A spark form opening and closing the door or from the compressor motor could cause an explosion with these refrigerators and freezers if flammables are stored in them. Flammable liquids for our purposes are liquids that have a boiling point less than 200^{o}C and burn in air.

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- Broken glassware should be discarded as soon as possible if not repairable. Repairable broken glassware should be repaired as soon as possible. Glassware and bottles should not be placed on the floor where someone can trip on them.
- Electric cords and wires should be placed where they cannot be tripped on.
- Toxic chemicals should be disposed of when they will no longer be used.
- Solvents should be stored in cabinets provided for this purpose (painted yellow). When in use, the common solvents should be in cans (painted red or stainless steel). These cans are filled from solvent drums located in the basement stockrooms. Solvent cans should be taken to the second floor stockroom for filling, following Department Training.
- Researchers must never work with hazardous substances when alone (outside normal hours). Overnight operations must be designed to prevent accidental release of hazardous chemicals by taking appropriate measures, e.g. automatic water turn off devices, wiring of condenser tubing, arranging for periodic inspection of the experiment, etc.

General Principles

- Be prepared for any accident or eventuality such as a fire, explosion, power failure, etc. Decide in advance what emergency action to take.
- Determine in advance the potential hazards that may be involved with chemicals to be handled and take appropriate preventative measures.
- Avoid all skin contact with hazardous chemicals and conduct your experiments in the hood to prevent inhalation of such chemicals.
- Always assume new compounds and those of unknown toxicity are hazardous and/or toxic.
- Drinking and eating are permitted only in offices and other non-laboratory areas.
- Eye protection is required at all times in the laboratory where chemicals are stored and handled and in shop areas.
- Horseplay, pranks or other acts of mischief are especially dangerous and are absolutely prohibited.
- Avoid skin contact, ingestion and inhalation of hazardous substances. Wearing of gloves, use of aspirators or pipette bulbs (never mouth suction) for filling pipettes, and washing hands after work are important preventive measures you must take when working with hazardous materials. In addition, to prevent inhalation of toxic vapors, gases, and mists, conduct all experiments in fume hoods as discussed earlier.

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Part VIII – Disposal and Handling of Chemicals

Department Guidelines for Disposal of Waste Solvents and Chemicals

Waste Organic Solutions

- Research chemists should segregate these into
  1) halogenated solvents
  2) non-halogenated solvents
  3) acid waste
  4) basic waters
  5) reductants
  6) oxidants

- Non-halogenated and relatively unreactive solvents, such as ethers, hydrocarbons, and nitriles may be incorporated with the halogenated solvent container when such contamination is unavoidable (e.g. residual solvents from HPLC runs).

- Labels must contain:
  1) name of researcher
  2) date that accumulation of waste began
  3) lab room number
  4) chemicals in bottle (Do not use abbreviations or figures.)
  5) approximate amounts of each chemical

- Use as small a container as is reasonable. Waste disposal is charged by weight.

- Mercury waste must be stored separately. Keep volumes to a minimum.

- Chemists should deliver the waste solvents to the Storeroom Manager.

- Group Safety representatives are responsible for transferring waste and surplus chemicals to 2nd floor stockroom. This entails the following steps:
  1) Identifying and labeling the principal hazard and/or precaution to be aware of in disposal (e.g. carcinogen, radioactivity, peroxides, explosive, strong acids/bases, lachrymator, dermal irritant, flammable, etc.)
  2) Stockroom personnel will advise on how to package the waste.
  3) Compounds that are explosive should be kept in the possession of the user. The user knows best how to handle these compounds. After they are no longer being used, it is the responsibility of the user to dispose of them. A student or postdoctoral fellow, after completing his/her research at Marquette, should never leave behind explosives for others to deal with. If the researcher does not know how to destroy the explosive safely, he/she should contact the company that sold the explosive (e.g. Aldrich Chemical). The company usually can tell an inquirer how to dispose of the explosive.

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Drain Disposal of Chemicals

This advisory serves to remind all chemists that certain water-soluble organic chemicals may be flushed down a drain if mixed with at least 100 volumes of excess water. An organic compound is considered water soluble if it dissolves to the extent of at least 3% (e.g. 0.3 mL or 0.3 g in 10 mL H_2O). Compounds that boil below 50°C (even if water soluble), should not be poured down the drain because of the possibility of unacceptable vapor buildup in the sewer system. A prime example of this would be diethyl ether. In addition, malodorous chemicals should not be flushed down the drain. In general, we suggest that common low M.W. solvents, such as methanol, ethanol, isopropyl alcohol, and acetone be disposed of via a drain after dilution.

On inorganic chemicals, such as mineral acids and alkalies, it is highly preferable to neutralize same followed by water dilution before drain disposal. Dilute solutions of inorganic salts may be disposed via drain only if both cation and anion are listed in the second columns (relatively non-toxic) of Tables 6.1 and 6.2 shown on pages 78 and 79 of "Prudent Practices for Disposal of Chemicals from Laboratories". A summary of disposal procedures is given in Appendix 8.

Water insoluble compounds, lachrymators, amines, mercaptans and other odoriferous materials of those capable of converting to same or toxic types, monomers and highly flammable compounds should never be discharged into laboratory drains. Ethers normally should be disposed of as discussed above (non-halogenated category). When rotary-evaporating methylene chloride, it would be advisable to use a cold trap and condense as much methylene chloride as possible to minimize its discharge through the drain.

Additional examples of chemicals not to be discharged under any circumstances into laboratory drains: mercury and mercury salts, lead compounds, arsenic compounds, chromium compounds, cyanides, nickel salts and complexes, strong oxidizing agents-peroxides and all carcinogens and suspect carcinogens.

NOTE: Chloroform in the presence of basic materials may undergo highly exothermic and even explosive reactions. For similar reasons, avoid mixing chloroform with acetone in the presence of trace quantities of a base when packaging materials for disposal.

Transporting Hazardous Chemicals

Department policy mandates that hazardous chemicals and solvents be carried in approved secondary containers (with handles) made of rubber, metal or plastic. Bottles small enough to be carried in the palm of the hand can be transported by that method. Compressed gas cylinders need to be capped and restrained during transport.

Procedures for Handling Accidental Release and Spills of Hazardous Chemicals including Solvents

Spills must be cleaned up and confined promptly by the person responsible for the spill. If responsibility cannot be determined, then the Chemical Hygiene Officer will take appropriate action and designate a person or persons to help with the clean-up process. Spill control pillows, absorbents, neutralizing agents for acids and bases, as well as pails, brooms, etc. are available in second floor storeroom.

Chemical Hygiene Plan

Spills of a highly toxic substance require special handling. In this case, the person responsible should not attempt clean-up alone. Assistance from a supervisor and perhaps the Milwaukee Fire Department may be necessary.

If highly flammable solvents such as diethyl ether, THF, low boiling hydrocarbons are spilled, alert other laboratory personnel immediately. Turn off any spark producing equipment and mop up the spill promptly with spill control pillows.

Procedures for working with Flammable and Explosive Substances
Flammable Solvents

The heating in open vessels of all solvents except water must be carried out in a hood. Use of the hood is recommended for the heating of flammable solvents even when the apparatus is enclosed (reflux, distillation), especially when the quantities are significant. A steam bath, heating mantle, oil bath or similar device should be used, but never a flame.
NOTE: When heating a flammable solvent in the open (e.g. in an Erlenmeyer flask for recrystallization), use a steam bath if possible. Among common recrystallizing solvents, only heptane, toluene and acetic acid cannot be boiled this way. [Carbon disulfide deserves special care, as its auto ignition point is so low (100^{o} C) that even a steam bath may be capable of igniting it.] Note the Table of Solvent Properties.
Because some hotplates pose a dual fire hazard**, restrict their use for recrystallization to non-flammable solvents such as carbon tetrachloride and chloroform, solvents with relatively high flashpoints such as ethanol and solvents which boil too high for the steam bath. Do not use them with solvents such as diethyl ether, methanol, pentane, hexane, petroleum ether, benzene and tetrahydrofuran. If the solvent is flammable, be careful to operate the hotplate at the lowest practical temperature and to avoid placing the hot flask in front of the hotplate whence vapors can be drawn inside the device.

**A hotplate's surface temperature can easily exceed the auto ignition point of the solvent. On the "High" setting the Corning PC-351, for example, reaches a temperature of about 500^{o} C. Even if the surface temperature is cool enough, solvent vapors can be ignited by the thermostat, which sparks when it cycles. This requires only that the flash point be reached; a condition that is met below room temperature for every common (flammable) recrystallizing solvent except acetic acid.

Chemical Hygiene Plan

Properties of Some Flammable Solvents

Compound	Boiling Point (°C)	Flash Point (°C)	Auto ignition Point
Acetic Acid	118	+40	465
Acetone	56	-17.8	538
Acentonitrile	82	+5	524
Benzene	80	-11	562
Carbon disulfide	46	-30	100
Ethanol	79	12.8	793
Diethyl ether	35	-45	180
Ethyl acetate	77	+7	427
Isopentane	29	-56	420
Isopropanol	83	-12	399
n-Heptane	98	-4	223
n-Hexane	69	21.7	248
Methanol	65	-11	470
n-Pentane	35	-40	309
Tetrahydrofuran	66	-17	321
Toluene	111	+4.4	480

Explosive and Flammable Substances

Any work with explosive materials mandates the use of protective equipment, such as face shields (with snap-on throat protector), gloves and safety shields.

Of the explosive materials handled in the Department laboratories, organic peroxides are the most frequently used and are also among the most dangerous because of their extreme sensitivity to shock, friction, heat, light, oxidizing and reducing agents. Be wary of peroxides contained in screw cap bottles. Twisting the cap may cause an explosion and fire. Organic peroxides are also highly flammable.

Chemical Hygiene Plan

Commercially purchased peroxides, such as benzoyl peroxide, t-butyl hydroperoxide, etc., are best stored in a flammable storage or suitably modified refrigerator. Compounds that form peroxides by an autoxidation process are aldehydes, ethers with primary and/or secondary alkyl groups (including acyclic and cyclic types, ketals and acetals), hydrocarbons with allylic, benzylic or propargylic hydrogens, conjugated dienes, enzymes and diynes and saturated hydrocarbons with tertiary hydrogens. Examples of especially dangerous peroxide formers are diisopropyl ether, diethyl ether, THF, divinylacetylene, decalin and 2,5 dimethylhexane. (See Appendix 7)

Because the above classes form peroxides as a result of exposure to 02 or other oxidizers, always store such substances in an inert atmosphere by flushing the container with an inert gas such as N2. Oxidation inhibitors (hydroquinone, etc.) should be added to the vessel when it seems appropriate.

Do not distill a known peroxide former before testing for peroxides by adding 0.5 ml. of the sample to a mixture of 1 mL of 10% KI solution and 0.5 mL of dil. HCl to which has been added a few drops of starch solution just prior to the test. A blue or blue black color will appear within a minute or so if peroxides are present.

Procedures for Handling Chemicals that Pose Hazards Because of Acute Toxicity, Chronic Toxicity or Corrosiveness

All work with these substances must be confined to designated laboratory areas such as a given laboratory, laboratory area or a fume hood. The designated areas must be posted with appropriate warning signs.

The listings for carcinogens, select carcinogens, reproductive toxins as well as that for corrosive substances are in this document.

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

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

Chemical Hygiene Plan

An excellent guideline for the procedures and precautions to take when working with these substances is given in "Prudent Practices, Chapter I.B., pp. 30-50."

In order to destroy small quantities ($\leq$ 25 g) of peroxides, dilute the sample with water to a concentration of 0.2% and transfer same to an aqueous solution of ferrous sulfate or sodium bisulfite. Use only a polyethylene container in this reduction process. For destruction of larger quantities, contact the Biosafety Office.

In addition to the peroxide forming chemicals noted above, compounds containing the following functional groups are sensitive to heat and shock: acetylide, azide, diazo, halamine, nitroso and ozonide. (See Appendix 3.) Diazomethane may decompose violently even when exposed to a ground glass joint. Handle these materials with extreme care. Chemicals with nitro group functionality may be exceptionally energetic and reactive, especially if other groups such as halogens are present. Other functional groups such as perchlorates, chlorates, nitrates, bromates, chlorites and iodates - organic or inorganic - must be handled carefully particularly at elevated temperatures.

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

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.

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

In the course of handling any chemical, you must take care that this substance does not accidentally come in contact with another material with which it is incompatible. (See Appendix 3.) If contact is made, a serious accident could ensue-explosion, fire or generation of a highly toxic or corrosive product.

Chemical Hygiene Plan

APPENDICES AND ATTACHMENTS

Chemical Hygiene Plan

Marquette University
Chemistry Department

NOTE: Insert CARBON form between sheets before filling out this Report.

ACCIDENTAL INJURY REPORT

Time and Place of Accident____

NAME of Injured Person____

Was Injured person a Student? Yes_____ No_____ Course #_______ Lab Section______Room_________

NAME and Category of Supervisor____
(Teaching Assistant, Faculty, etc.)

DESCRIBE Accident (include the injured's activity, equipment and/or chemicals used and part of the body injured and by what)

____
____
____
____
____

Nature and Extent of Injury____
____

Type of First-Aid, by____

Student Health Center? Yes__________ No___________

Hospital Treatment? Yes__________ No__________ Name of Hospital___________________________

Principal Cause(s) of Accident and Injury____
____
____
____

Aggravating Causes____
____
____

What should be done and by whom to prevent a recurrence of this or similar accidents?

____
____
____
____

Signature of Injured Person____ Date___________________

Report Filed by____ Date_____________________

Please give this Report to the Lab Coordinator.

Chemical Hygiene Plan

Marquette University
Department of Chemistry
August 14, 2001

TO: Chemistry Faculty and Teaching Assistants

SUBJECT: Eye Protection

Safety in the laboratory is one of the most important aspects in the training of any individual. Among the safety practices, prevention of injury to the eyes is of perhaps the greatest importance, both because of the probability of such injuries and because of the tragic consequences in the case of a permanent injury. Yet, in most cases, such injuries could have been prevented simply by wearing protective equipment.

We shall continue the following practices:

1) All Teaching Assistants are instructed and authorized to dismiss any student now wearing safety goggles or other suitable protective equipment from the laboratory. (If a student forgot his/her personal safety goggles, he/she should go to the stockroom to borrow an emergency pair of use on that day.)
2) All Teaching Assistants are instructed to report to the Departmental Office any student who causes him/her any problems in enforcing this rule. An example might be a student who repeatedly removes his/her goggles in the laboratory.
3) All instructional staff without exception are expected to enforce the above practices.

Charles Wilkie
Chair & Professor

Acknowledgement by Teaching Assistants:

I have received a copy of this notice and understand it. I also understand that a similar notice [1) and 2) above] will be posted in the undergraduate laboratory where I am the laboratory instructor.

____

Chemical Hygiene Plan

Appendix 3
POTENTIALLY EXPLOSIVE CHEMICALS AND REAGENT COMBINATIONS

Table F.1 lists some common classes of laboratory chemicals that have potential for producing a violent explosion when subjected to shock or friction. These chemicals should never be disposed of as such.

Table F.2 lists a few illustrative combinations of common laboratory reagents that can produce explosions when they are brought together or that give reaction products that can explode without any apparent external initiating action.

Table F.1 Shock-Sensitive Compounds

Acetylenic compounds, especially polyacetylenes, haolacetylenes and heavy metal salts of acetylenes (copper, silver and mercury salts are particularly sensitive)
Acyl nitrates
Alkyl nitrates, particularly polyol nitrates such as nitrocellulose and nitroglycerine
Alkyl and acyl nitrites
Alkyl perchlorates
Ammine metal oxosalts: metal compounds with coordinated ammonia, hydrazine or similar nitrogenous donors and ionic perchlorate, nitrate, permanganate or other oxidizing group
Azides, including metal, nonmetal and organic azides

Chlorite salts of metals, such as $AgClO_2$ and $Hg(ClO_2)$

Diazonium salts, when dry

Fulminates (silver fulminate, AgCNO, can form in the reaction mixture from the Tollens' test for aldehydes if it is allowed to stand for some time; this can be prevented by adding dilute nitric acid to the test mixture as soon as the test has been completed.)

Hydrogen peroxide becomes increasingly treacherous as the concentration rises above 30%, forming explosive mixtures with organic materials and decomposing violently in the presence of traces of transition metals.

N-Halogen compounds such as difluoroamino compounds and halogen azides
N-Nitro compounds such as N-nitromethylamine, nitrourea, nitroguanidine and nitric amide.

Oxo salts of nitrgeneous bases: perchlorates, dichromates, nitrates, iodates, chlorites, chlorates and permanganates of ammonia, amines, hydroxylamine, guanidine, etc.

Chemical Hygiene Plan

Perchlorate salts. Most metal, nonmetal and amine perchlorates can be detonated and may undergo violent reaction in contact with combustible materials.

Peroxides and hydroperoxides, organic

Peroxides (solid) that crystallize from or are left from evaporation of peroxidizable solvents

Peroxides, transition-metal salts

Picrates, especially salts of transition and heavy metals, such as Ni, Pb, Hg, Cu and Zn; picric acid is explosive but is less sensitive to shock or friction than its metal salts and is relatively safe as a water-wet paste.

Polynitroalkyl compounds such as tetranitromethane and dinitroacetonitrile

Polynitroaromatic compounds, especially polynitro hydrocarbons, phenols and amines

---

Table F.2 Potentially Explosive Combinations of Some Common Reagents

---

Acetone + chloroform in the presence of base

Acetylene + copper, silver, mercury or their salts

Ammonia (including aqueous solutions) + Cl_2, Br_2 or I_2

Carbon disulfide + sodium azide

Chlorine + an alcohol

Chloroform or carbon tetrachloride + powdered Al or Mg

Decolorizing carbon + an oxidizing agent

Diethyl ether + chlorine (including a chlorine atmosphere)

Dimethyl sulfoxide + an acyl halide, $SOCl_2$ or $POCl_3$

Dimethyl sulfoxide + CrO_3

Ethanol + calcium hypochlorite

Ethanol + silver nitrate

Nitric acid +acetic anhydride or acetic acid

Picric acid + a heavy-metal salt, such as of Pb, Hg or Ag

Silver oxide + ammonia + ethanol

Sodium + a chlorinated hydrocarbon

Sodium hypochlorite + an amine

Chemical Hygiene Plan

APPENDIX 4

Classes of Carcinogenic Compounds (*select carcinogens)

Alkylating agents: ∀-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: epoxies
**ethylenimine*
2-rnethylaziridine

Alkylating agents: diazo, azo, and azoxy compounds
4-dimethylaminoazobenzene

Alkylating agents: electrophilic alkenes and alkynes
**acrylonitrile*
acrolein
ethyl acrylate

Acylating agents
∃-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-dibromo ethane
1,4-dichlorobenzene
1,2-dichloroethane
2,2-dichloroethane
1,3-dichloropropene
hexachlorobenzene

methyl iodide
tetrachloroethylene
trichloroethylene
2,4,6-trichlorophenol

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

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

Aromatic amines
**4-aminobiphenyl*
**benzidine (p,p'-diaminobiphenyl)*
**∀-napthylamine*
**∃-napthylamine*
aniline
o- anisidine (2-methoxyaniline)
2,4-diaminotoiuene
o- toluidine

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

Natural products (including antitumor drugs)
adriamycin
aflatoxins
bleomycin
cisplatin
progesterone
reserpine
safrole

Miscellaneous organic compounds
**formaldehyde (gas)*
acetaldehyde
1,4-dioxane
ethyl carbamate (urethane)
hexamethylpyhosphoramide
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

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
Alkali and Alkaline earth carbides hydrides hydroxides metals oxides peroxides	Water Acids Halogenated organic compounds Halogenating agents Oxidizing agents
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, heavy metals and their salts, oxidizing agent

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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, strong bases
Decaborane	Carbon tetrachloride and some other halogenated hydrocarbons
Flammable liquids	Ammonium nitrate, chromic acid, hydrogen peroxide, nitric acid, sodium peroxide, halogens
Fluorine	Everything
Hydrocarbons (such as butane, propane, benzene)	Fluorine, chlorine, bromine, chromic acid,sodium peroxide
Hydrocyanic acid	Nitric acid, alkali
Hydrofluoric acid (anhydrous)	Ammonia (aqueous or anhydrous)
Hydrogen peroxide	Copper, chromium, iron, most metals or their salts, alcohols, acetone, organic materials, aniline, nitromethane, combustible materials
Hydrogen sulfide	Fuming nitric acid, oxidizing gases
Hypochlorites	Acids, activated carbon

Iodine	Acetylene, ammonia (aqueous or anhydrous), hydrogen
Mercury and its amalgams	Acetylene, fulminic acid, ammonia, nitric acid and sodium oxize
Nitrates	Sulfuric acid
Nitric acid (concentrate)	Acetic acid, aniline, chromic acid, chromates, hydrocyanic acid, hydrogen sulfide, flammable liquids, flammable gases, copper, brass, any heavy metals, permanganates, sulfides, sulfuric acid
Nitrites	Acids, oxidizing agents
Nitroparaffins	Inorganic bases, amines
Oxalic acid	Silver, mercury and their salts
Oxygen	Oils, grease, hydrogen, flammable liquids, solids, or gases
Perchloric acid	Acetic anhydride, bismuth and its alloys, alcohol, paper, wood, grease, oils
Peroxides, organic	Acids (organic or mineral), avoid friction, store cold
Phosphorous (white)	Air, oxygen, alkalis, reducing agents
Phosphorus pentoxide	Alcohols, strong bases, water
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 peroxide	Ethyl or methyl alcohol, glacial acetic acid,acetic anhydride, benzaldehyde, carbon disulfide, glycerine, ethylene glycol, ethyl acetate, methyl acetate, furfural

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Sulfides	Acids
Sulfuric acid	Potassium chlorate, potassium perchlorate, potassium permanganate, (similar compounds of light metals such as sodium, lithium)
Tellurides	Reducing agents

Chemical Hygiene Plan

APPENDIX 5

Chemicals that React Explosively with Water

This appendix lists some common laboratory chemicals that react violently with water and that should always be stored and handled so that they do not come into contact with liquid water or water vapor. They are prohibited from landfill disposal, even in a lab pack, because of the characteristic of reactivity. Procedures for decomposing laboratory quantities can be obtained from the Safety Committee Chairman.

Alkali metals
Alkali metal hydrides
Alkali metal amides
Metal alkyls, such as lithium alkyls and aluminum alkyls
Grignard reagents
Halides of nonmetals, such as BCl_3, BF_3, PCl_3, PCl_5, $SiCl_4$, S_2Cl_2
Inorganic acid halides, such as $POCl_3$, $SOCl_2$, $S0_2Cl_2$
Anhydrous metal halides, such as $AlCl_3$, $TiCl_4$, $ZrCl_4$, $SnCl_4$
Phosphorous pentoxide
Calcium carbide
Organic acid halides and anhydrides of low molecular weight

Chemical Hygiene Plan

APPENDIX 6

Chemicals that React Explosively with Air

Many members of the following readily oxidized classes of common laboratory chemicals ignite spontaneously in air. Pyrophoric chemicals should be stored in tightly closed containers under an inert atmosphere (or, for some, an inert liquid), and all transfers and manipulations of them must be carried out under an inert atmosphere or liquid. Pyrophoric chemicals cannot be put into a landfill because of the characteristic of reactivity. Suggested disposal procedures can be obtained from the Safety Committee Chairman.

Grignard reagents, RMgX
Metal alkyls and aryls, such as RLi, RNa, R_3Al, R_2Zn
Metal carbonyls, such as $Ni(CO)_4$, $Fe(CO)_5$, $Co_2(CO)_8$
Alkali metals such as Na, K
Metal powders, such as Al, Co, Fe, Mg, Pd, Pt, Ti, Sn, Zn, Zr
Metal hydrides, such as NaH, $LiAlH_4$
Nonmetal hydrides, such as B_2H_6 and other boranes, PH_3, AsH_3
Nonmetal alkyls, such as R_3B, R_3P, R_3As
Phosphorus (white)

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APPENDIX 7

Peroxide Forming Chemicals

Many common laboratory chemicals can form peroxides when allowed access to air over a period of time. A single opening of a container to remove some of the content can introduce enough air for peroxide formation to occur. Some types of compounds form peroxides that are treacherously and violently explosive in concentrated solution or as solids. Accordingly, peroxide-containing liquids should never be evaporated to dryness. Peroxide formation can also occur in many polymerizable unsaturated compounds, and these peroxides can initiate a runaway, sometimes explosive polymerization reaction. Procedures for testing for peroxides and for removing small amounts from laboratory chemicals are available from the Safety Committee Chairman.

This appendix provides a fist of structural characteristics in organic compounds that can peroxidize and some common inorganic materials that form peroxides. Although the tabulation of organic structures may seem to include a large fraction of the common organic chemicals, they are listed in an approximate order of decreasing hazard. Reports of serious incidents involving the last five organic structural types are extremely rare, but they are included because laboratory workers should be aware that they can form peroxides that can influence the course of experiments in which they are used.

This appendix also provides specific examples of common chemicals that can become serious hazards because of peroxide formation. Suggested time limits are given for retention or testing of these compound after opening the original container. Although some laboratories mark containers of such chemicals with the date of receipt of the original container, it should be recognized that such dating does not take into account the unknown time span between original packaging of the chemicals and its date of receipt. The date of opening the original container of a chemical that is a hazardous peroxide-former should always be marked on the container. Labels such as that illustrated below should be provided to all laboratory workers to affix to and date all samples of peroxide-forming reagents that they receive.

Table 1.2 gives examples of common laboratory chemicals that are prone to form peroxides on exposure to air. The lists are not exhaustive, and analogous compounds that have any of the structural features given in Table 1.1 should be tested for the presence of peroxides before being used as solvents or being distilled. The recommended retention times begin with the date of synthesis or of opening the original container.

PEROXIDIZABLE COMPOUND

Date	Received	Opened
	__________	__________

Discard or Test Within 6 Months after Opening

Table 1.1 Types of Chemicals That are Prone to Form Peroxides		
1.	C -- O --	Ethers and acetals with ∀ atoms
2.	C = C -- C -- H	Olefins with allylic hydrogen atoms
3.	C = C -- X	Chloroolefins and fluoroolefins
4.	CH2 = C	Vinyl halides, esters, and ethers
5.	C = C -- C C	Dienes
6.	C = CHC CH	Vinylacetylenes with ∀ hydrogen atoms
7.	H- - C -- C CH	Alkylacetylenes with ∀ hydrogen atoms
8.	H -- C -- Ar	Alkylarenes that contain tertiary hydrogen atoms
9.	C--H	Alkanes and cycloalkanes that contain tertiary hydrogen atoms
10.	C C -- C02R	Acrylates and methacrylates
11.	C -- OH	Secondary alcohols
12.	O C -- C -- H	Ketones that contain ∀ hydrogen atoms
13.	H -- C O	Aldehydes
14.	O C -- NH -- CH	Ureas, amides, and lactams that have a hydrogen atom on a carbon atom attached to nitrogen

B. Inorganic Substances.

1. Alkali metals, especially potassium, rubidiium, and cesium
2. Metal aides
3. Organometallic compounds with a metal atom bonded to carbon
4. Metal alkoxides

Chemical Hygiene Plan

Table 1.2 Common Peroxide-Forming Chemicals

LIST A

Severe Peroxide Hazard on Storage with Exposure to Air

Discard within 3 months

Diisopropyl ether (isopropyl ether)	Sodium amide (sodamide)
Divinylacetylene (DVA)	Vinyladene Chloride (1,1-dichloroethylene)
Potassium metal	
Potassium amide	

LIST B

Peroxide Hazard on Concentration; Do Not Distill or Evaporate Without First Testing for the Presence of Peroxides.

Discard or test for peroxides after 6 months

Acetaldehyde diethyl acetal (acetal)	Diacetylene (butadiene)
Cumene (isopropylbenzene)	Dicyclopentadiene
Cyclohexane	Diethyl ether (ether)
Cyclopentene	Diethylene glycol dimethyl ether (diglyme)
Decalin (decahydronaphthalene)	Furan
Dioxane	Methylacetylene
Ethylene glycol dimethyl ether (glyme)	Methylcyclopentane
Ethylene glycol ether acetates	Methyl isobutyl ketone
Ethylene glycol monoethers (cellosolves)	Tetrahydrofuran (THF)
	Tetralin (tetrahydronaphthalene)
	Vinyl ethers[a]

LIST C

Hazard of Rapid Polymerization Initiated by Internally Formed Peroxides[a]

a. Normal liquids. Discard or test for peroxides after 6 months

Chloroprene (2-Chloro-1,3-butadiene)[c]	Vinyl acetate
Styrene	Vinylpyridine

b. Normal Gases; Discard after 12 months d

Butadiene[c]	Vinylacetylene (MVA)[c]
Tetraluoroethylene (TFE)[c]	Vinyl chloride

APPENDIX 8 Guidelines for Disposal of Chemicals in the Sanitary Sewer System

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The following lists comprise compounds that are suitable for disposal down the drain with excess water in quantities up to about 100 g at a time. However, local regulations may prohibit drain disposal of some and should be checked before any laboratory compiles its list of compounds acceptable for disposal down its drains. Compounds on both lists are water soluble to at least 3% and present low toxicity hazard. Those on the organic list are readily biodegradable.

1. ORGANIC CHEMICALS

Alcohols:
Alkanols with less than 5 carbon atoms
t-Amyl alcohol
Alkanediols with less than 8 carbon atoms
Glycerol
Sugars and sugar alcohols
Alkyoxyalkanols with less than 7 carbon atoms
n-$C_4H_9OCH_2CH_20CH_2CH_20H_2$
2-Chloroethanol

Aldehydes:
Aliphatic aldehydes with less than 5 carbon atoms

Amides:
$RCONH_2$ and RCONHR with less than 5 carbon atoms
$RCONR_2$ with less than 11 carbon atoms

Amines[a]:
Aliphatic amines with less than 7 carbon atoms
Aliphatic diamines with less than 7 carbon atoms
Benzylamine
Pyridine

Carboxylic Acids:
Alkanoic acids with less than 6 carbon atoms[a]
Alkanedioic acids with than than 8 carbon atoms
Hydroxyalkanoic acids with less than 6 carbon atoms
Aminoalkanoic acids with less than 7 carbon atoms
Ammonium, sodium, and potassium salts of the above acid classes with less than 21 carbon atoms
Chloroalkanedioic acids with less than 4 carbon atoms

Esters:
Esters with less than 5 carbon atoms

Isopropyl acetate

Ethers:
Tetrahydrofuran
Dioxolane
Dioxane

[a] Polymerizable monomers should be stored with a polymerization inhibitor from which the monomer can be separated by distillation just before use.

[b] Although common acrylic monomers such as acrylonitrile, acrylic acid, ethyl acrylate, and methyl methacrylate can form peroxides, they have not been reported to develop hazardous levels in normal use and storage.

[d] Although air will not enter a gas cylinder in which gases are stored under pressure, these gases are sometimes transferred from the original cylinder to another in the laboratory, and it is difficult to be sure that there is no residual air in the receiving cylinder. An inhibitor should be put into any such secondary cylinder before one of these gases is transferred into it; the supplier can suggest inhibitors to be used. The hazard posed by these gases is much greater if there is a liquid phase in such a secondary container, and even inhibited gases that have been put into a secondary container under conditions that create a liquid phase should be discarded within 12 months.
[a] Those with a disagreeable odor, such as dimethylamine, 1,4-butanediamine, butyric acids, and valeric acids, should be neutralized, and the resulting salt solutions flushed down the drain, diluted with at least 1000 volumes of water.

Ketones:
Ketones with less than 6 carbon atoms

Nitrites:
Acetonitrile
Propionitrile

Sulfonic Acids:
Sodium or potassium salts of most are acceptable

II. Inorganic Chemicals

This list comprises water-soluble compounds of low-toxic-hazard cations and low-toxic-hazard anions. Compounds of any of these ions that are strongly acidic or basic should be neutralized before disposal down the drain.

Cations	Anions
Al^{3+}	BO_3^{3-}, $B_4O_7^{2-}$
Ca^{2+}	Br^-
Cu^{2+}	CO_3^{2-}
$Fe^{2+,3+}$	Cl^-

Chemical Hygiene Plan

H^{+}	$HS0_3^{-}$
K^{+}	OCN^{-}
Li^{+}	OH^{-}
Mg^{2+}	I^{-}
Na^{2+}	NO_3^{-}
NH^{4+}	PO_4^{3-}
Sn^{2+}	$S0_4^{2-}$
Sr^{2+}	SCN^{-}
$Ti^{3+,4+}$	
Zn^{2+}	
Zr^{2+}	

Glove Compatibility Chart

Resistance to Chemicals of Common Glove Materials

(E = Excellent, G = Good, F = Fair, P = Poor)

Chemical	Natural Rubber	Neoprene	Nitrite	Vinyl
Acetaldehyde	G	G	E	G
Acetic acid	E	E	E	E
Acetone	G	G	G	F
Acrylonitfile	P	G	-	F
Ammonium hydroxide sat.	G	E	E	E
Aniline	F	G	E	G
Benzaldehyde	F	F	E	G
Benzene*	P	F	G	F
Benzyl chloride*	F	P	G	P
Bromine	G	G	-	G
Butane	P	E	-	P
Butyraldettyde	P	G	-	G
Calcium hypochlorite	P	G	G	G
Carbon disulfide	P	P	G	F
Carbon tetrachloride*	P	F	G	F
Chlorine ~	G	G	-	G
Chloroacetone	F	E	-	P
Chloroform*	P	F	G	P
Chromic acid	P	F	F	E
Cyclohexane ~	F	E	-	P
Dibenzyl ether	F	G	-	P
Dibutyl phthalate	F	G	-	P
Diethanolamine	F	E	-	E
Diethyl ether	F	G	E	P
Dimethvl sulfoxide	NO DATA AVAILABLE,	USE	BUTYL RUBBER	GLOVES**
Ethyl acetate	F	G	G	F
Ethylene dichloride	P	F	G	P
Ethylene glycol	G	G	E	E
Ethylene trichlor-ide	P	P		P
Fluorine	G	G	-	G
Formaldehyde	G	E	E	E
Formic acid	G	E	E	E

continued

Chemical	Natural Rubber	Neoprene	Nitrite	Vinyl
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 cellosolve	F	E	-	P
Methyl chloride*	P	E	-	P
Methyl ethyl ketone	F	G	G	P
Methylene chloride	F	F	G	F
Monomethanolamine	F	E	-	E
Morpholine	F	E	-	E
Naphthalene*	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 cone.	G	G	F	G
Toluene*	P	F	G	F
Trichloroethylene*	P	F	G	F
Tricresyl phosphate	P	F	-	F
Triethanolarnine	F	E	E	E
Trinitrotoluene	P	E	-	P

* aromatic and halogenated hydrocarbons attack alt types of natural and synthetic glove material. When swelling occurs, change to fresh gloves and allow the swollen gloves to dry and return to normal.

** No data on the resistance to dimethyl sulfoxide of natural rubber, neoprene, nitrite rubber or vinyl materials is available; the manufacturer of the substance recommends the use of butyl rubber gloves.