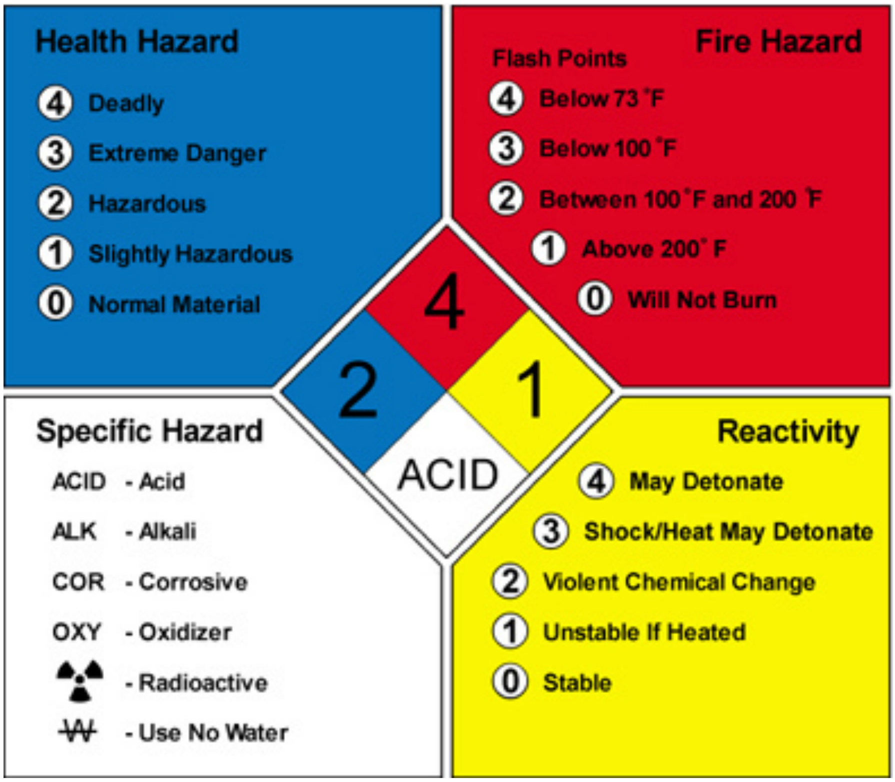


CHEMICAL SAFETY MANUAL

FOR THE DIVISION OF CHEMISTRY AND CHEMICAL ENGINEERING

California Institute of Technology

CCE Chemical Safety Manual Table of Contents

Appendices

Revised Fall, 2013

I. Safety plan for the Division of Chemistry and Chemical Engineering

Training in Safety is required for everyone in the CCE Division. Before being issued a key and beginning work, each new member must have documented training in the following areas. Training is provided at Three Levels for new employees:

1. **Safety Orientation - for all new employees, including office staff**
    - Safety organization structure
    - Right to know
    - Medical trips and reporting
    - Safety equipment
    - *Evacuation plan for fire and earthquake**
    (http://www.safety.caltech.edu/services/emergency)
2. **Laboratory Safety - for researchers in chemical laboratories**
    - Safety equipment available
    - Films on proper practice
    - Electrical Equipment spark/hazards
    - Labeling of chemicals
    - Chemical disposal
    - Spill Clean up
    - Inspection procedure
        - Routine
        - Prestart up inspection
    - Chemical Hazard
        - Hazard classification guide
        - Carcinogen, tetragen
3. ***Group Safety - procedures will be developed by each research group***
    - *Biological hazards**
    - *Vacuum line**

*Disposal procedures**
*Stock room**
*Safety meetings**
*Hazard awareness and update**

**These topics are described in other documents. (Other issues of chemical hygiene will be addressed by the Institute Safety Office).*

The Caltech Environment, Health and Safety Office (referred to in this Manual as the Safety Office) offers manuals in safety areas such as the Hazardous Waste Management Reference Guide, Laser Safety Manual and the Radiation Safety Training and Reference Manual. Contact the Caltech Safety Office for these other manuals.

II. CCE Division Safety Organization

CCE Division Chair: The CCE Division Chair has ultimate responsibility for safety in the CCE Division. The CCE Division Chair appoints the appropriate committees, provides support for safety equipment, and enforces compliance in the Division.

CCE Division Safety Liaison/Coordinator: The CCE Safety Liaison works directly with {EH&S) Environmental Health and Safety to oversee that all CCE labs comply with all Institute policies and procedures regarding lab safety. EH&S and the CCE Safety Liaison meet weekly to discuss policies and procedures to better serve CCE as a Division. Weekly lab inspections are done continually with each Lab Safety Officer to help ensure the safety for those working in the labs. The Safety Liaison reports directly to the Division Administrator.

CCE Division Safety Committee: This committee will advise the Division Chair on items of policy. This group will work with the Institute Safety Office to maintain the safety education and inspection program.

Laboratory Supervisor (**Principal Investigator**): Each faculty member is directly responsible for compliance of the members of his/her group with the CCE Division and Institute safety procedures and for developing a plan for any special hazards involved in the research conducted by his or her group.

Group Safety Officer: In each group, a safety officer is appointed. This person will advise the laboratory supervisor on issues required to maintain a safe lab environment, rectify deficiencies identified in safety inspections, and will also train new researchers in the group safety procedures. Group safety officers function as floor wardens as part of the Emergency Evacuation Plan

Researchers: Each researcher must complete the training program and comply with the safety requirements of the CCE Division.

III. Hazard Communication Regulations and OSHA Lab. Standard

On November 25, 1983, the federal Occupational Safety and Health Administration (OSHA) promulgated a final standard entitled "Hazard Communication". To meet federal requirements, the California Occupational Safety and Health Administration (CAL/OSHA) issued its own "Hazard Communication Standard" with some requirements unique to California (reference: Title 8, California Administrative Code, section 5194, General Industry Safety Orders). The purpose of this standard is to ensure that the hazards of all chemicals are evaluated and that information concerning them is communicated to affected employers and employees. The basis for both the California and federal standard is the Material Safety Data Sheet (MSDS).

All persons who may be exposed to hazardous chemicals under normal working conditions or in foreseeable emergencies are to be instructed in requirements of the standard. Workers such as office staff who encounter hazardous chemicals only in non-routine, isolated instances are not required to be instructed in the requirements of the standard.

A hazardous material is any chemical or mixture of chemicals that represents a potential danger to the individual, equipment or property. Hazardous materials are generally classified as physical hazards, acute health hazards, or chronic health hazards.

Physical hazards include:

- Combustible materials
- Compressed gases
- Explosive substances
- Flammable gases, liquids, and aerosols
- Organic peroxides
- Oxidizers
- Pyrophoric materials
- Reactive materials

Acute health hazards include:

- Acute toxins
- Irritants
- Anesthetics and narcotics
- Corrosive materials

Asphyxiates
Infectious biological agents

Chronic health hazards include:

Carcinogens
Chronic toxins
Ionizing radiation
Mutagens
Sensitizers
Target-organ toxins
Teratogens

(A) Supervisor Responsibility

Laboratory supervisors have specific legal responsibilities relating to hazardous materials under the provisions of the CAL/OSHA Hazard Communication Standard. These include informing and/or training new and existing employees of:

1. Requirements of the CAL/OSHA Hazard Communication Standard

2. Any work area where hazardous materials are present

3. The methods used to detect the presence or release of a hazardous material

4. The physical and health hazards of classes of hazardous chemicals in the work area

5. The measures employees can take to protect themselves from these hazards

6. How employees can obtain and use the appropriate hazard information

For research laboratories only, CAL/OSHA allows this training to be conducted by *classes* of hazardous materials and does not necessarily have to be specific to individual chemicals. It is the responsibility of each supervisor, however, to be aware of the classes of hazardous materials in use in his/her area and to provide the proper information and equipment necessary for the safe handling of any hazardous material. This must include a thorough new employee orientation program and an ongoing safety education program for all employees.

It is the additional responsibility of each supervisor to see that all employees have access to the vendor – supplied Materials Safety Data Sheets (MSDS). MSDS forms are available in the Safety Office (Room 25 in Business Services Building-Keith Spalding Bldg). MSDS are also available at www.hazard.com.

(B) Employee Responsibility

Although employees have no specific legal obligations under the CAL/OSHA Hazard Communication Standard, each researcher has a personal and professional responsibility to use the many available resources to identify the hazards associated with any chemicals that may be used. The information is necessary to plan the proper use, storage, and disposal of all hazardous materials.

(C) OSHA Laboratory Standard

The CAL/OSHA Standard entitled "Occupational Exposures to Hazardous Chemicals in Laboratories" (Title 8, California Administrative Code, section 5191, General Industry Safety Order) became effective in 1991. The standard establishes the responsibilities of a "Chemical Hygiene Officer." The "Chemical Hygiene Plan" as defined in the legislation is fulfilled by the requirements of The Institute Safety Hygiene Plan and individual division safety plans.

This manual describes the standard operating procedures relevant to safety and health considerations to be followed when laboratory operations in chemistry and chemical engineering involve the use of hazardous chemicals.

The Federal OSHA and CAL/OSHA Laboratory Standards are available at the Campus Safety Office.

IV. Injuries/Illnesses

Emergencies, work related or non-work-related: Contact Security at extension 5000.

Work related: The Institute provides Workers' Compensation Insurance to all Institute employees, including staff, students on the payroll, approved volunteers and Professors Emeritus, for expenses incurred from illness or injury arising out of and in the course of their employment at the Institute.

Non-work-related: The employee shall utilize his/her personal medical physician and private medical insurance. In cases of emergency, follow procedure below with the exception that the employee shall provide private medical insurance information to the medical provider.

(A) Reporting requirements for work-related injuries/illnesses

Employees should report the injury to their supervisor immediately. Thereafter, the supervisor and/or employee will notify the Disability & Leave Administration Unit at extension 4577 so that an Employee Claim Form for Workers' Compensation Benefits and an Employee Accident Report Form can be issued to the injured worker within 24 hours of knowledge of the injury. The injured employee shall complete and return both forms to the Disability & Leave Administration Unit within three (3) working days of their receipt of the forms. The supervisor shall complete the Supervisor Injury Investigation Report and return the original signed form to the Disability & Leave Administration Unit within three (3) working days of knowledge of the injury. The Supervisor Injury Investigation Report can be obtained from the Human Resources Webpage, using the following link: http://cit.hr.caltech.edu/InjuryInvestigation.htm

(B) Medical Treatment for work-related injuries/illnesses

The following section describes appropriate response to injuries/illnesses in both emergency and non-emergency situations:

(1) In case of an emergency, contact Security at extension 5000 for paramedics. The employee will be taken to the Emergency Room at Huntington Memorial Hospital, located on Fairmount Avenue near Congress Street, in Pasadena, or another available local hospital emergency room if necessary. If work related, the hospital staff should be informed that the injury is work-related.

(2) In the case of a non-emergency, injured employees are referred to either:

(a) Huntington Hospital Occupational Health Center (H.O.H.C.), (626) 229-8989, 800 S. Fairmount Avenue (near the corner of Fairmount Avenue and Bellefontaine Street), Suite 312, Pasadena. The Center's hours are 7:30 a.m. to 5:00 p.m., Monday through Friday, or

(b) St. George Medical Clinic, (626) 440-0097, 1750 E. Colorado Blvd., Pasadena (2 blocks East of Pasadena City College). The Clinic's hours are 8:30 a.m. to 6:00 p.m., Monday through Friday.

The Disability & Leave Administration Unit, extension 4577, should be notified immediately so that the appropriate referral can be made and so the processing of necessary forms and benefits can be initiated.

(3) In the event an injury occurs outside of HOHC's or St. George's regular hours, weekend, or holiday, the injured employee should go to Huntington Hospital Emergency Room.

(4) For work related injuries, employees should not use their own doctor unless specified in writing prior to an injury occurring. Forms to pre-designate a doctor are available in the Disability & Leave Administration Unit of Human Resources.

(5) If the employee needs transportation, the department shall contact Security at extension 4701 to coordinate a taxi. Supervisors and co-workers' should not transport injured employee to the hospital due to general liability reasons.

(6) Caltech's Student Health Center shall treat minor first aid injuries for students only. Staff shall not utilize the Student Health Center. Any injuries requiring more than first aid treatment shall be referred to HOHC.

(7) In the case of chemical exposure, the employee should take a copy of the MSDS to the hospital.

(8) For first aid injuries, administer first aid as necessary.

V. Safety Equipment

The key items of safety equipment are:

(A) *Safety glasses* – Safety glasses must be worn at all times when working in a laboratory. The Division provides non-prescription safety glasses at no charge. **Non-prescription safety glasses** are available in the Crellin Stockroom. **Prescription safety glasses** are only available to arriving first-year graduate students in the Fall. The Division will pay for one pair and not be responsible for any lost or broken safety glasses. Prescription safety glasses or a referral can be obtained by presenting a copy of your current eyeglass prescription to Joe Drew or other stockroom personnel.

(B) *Apparel* – Lab coats and gloves must be worn at all times when handling hazardous materials. A lab coat may can be obtained through the VWR Stockroom; see Joe Drew in the Chemistry Stockroom for an authorization form for one coat per researcher at the time the researcher starts lab work. Gloves and replacement lab coats are the responsibility of the research group. Remove your gloves before leaving the lab, especially when going to a public area.

(**C)** *Safety shields* – The Division will arrange to construct lexan safety shields at lab benches and fume hoods. Contact Joe Drew.

(D) *Emergency Showers and eyewashes* – Are located throughout the labs and adjacent corridors. Know where the closest ones are.

(E) *Obtaining Respiratory Equipment* – The Caltech Safety Office issues respirators. The initial step is an evaluation of the operation or process taking place in the laboratory. Process and engineering controls are considered first before a respirator is recommended. Contact the Caltech Safety Office for the “Physical Status Questionnaire” to determine your ability to wear a respirator.

(F) *Carriers for 4-liter bottles* – Carriers must be used when carrying glass bottles of chemicals.

VI. Emergency Evacuation Assembly Areas

The assembly areas for CCE buildings during an emergency evacuation are as follows:

Braun Lab:	Grassy area west of the building near Wilson
Broad Center:	North side of Beckman Inst. lawn near Broad
Church Lab:	San Pasqual walkway north of Church
Crellin Lab:	Area north of Gates Annex Chem Library
Gates Annex:	Area north of Gates Annex Chem Library
Mead Lab:	South side Beckman Inst. lawn across Mead
Noyes Lab:	Courtyard east of Braun and south of Noyes
Schlinger Lab	North parking lot of Schlinger
Spalding Lab:	Lawn east of Spalding and north of Winnett
Fairchild Library subbasement:	Lawn east of Spalding and north of Winnett

VII. Viewing Safety Videos

One MUST view the safety video in order to complete the Section VII of the Safety Check-In form. One may see the video in the CCE Division Office or may view it at one's own computer on the Caltech campus. Contact the Division Office for the URL.

The strict policy of the Chemistry and Chemical Engineering Division is that Safety Check-In must be completed before an authorization for a key to an office or a lab will be issued.

For further information, see your group safety officer, the Graduate Option Administrator, or the Division Office.

VIII. Electrical Equipment

All electrical equipment purchased should be UL (Underwriter's Laboratory) approved. Refrigerators for storing flammable chemicals should be purchased as built by the manufacturer for flammable materials storage. Vacuum pumps must be delivered to the Electrical Shop (61 Crellin) upon receipt from the vendor for installation of proper on-off switches; the switches on pumps as manufactured are not adequate. Oil baths should be heated by temperature regulated hot plates. Do not heat oil baths with submerged wire heaters which are unsheathed and noninsulated. Such heaters are an electrical shock hazard and a source of ignition for oil bath fire. Paper clips used as stir bars may bridge across unsheathed heating wire causing a short-circuit and sparks.

Avoid ganging multi-port extension cords. If additional electrical outlets are needed, see Joe Drew, the Facilities Coordinator (Ext. 2745).

Locating electrical equipment in the vicinity of potentially flammable fumes must be done with care. Some vapors are heavier than air and may diffuse along the floor and ignite when exposed to electrical wiring. Ovens and incubators, for example, should be elevated. Any questions should be referred to the CCE Electrical Shop (Ext. 6514).

IX. Hazardous Waste Disposal

For the purposes of this program, a “waste” is defined as a material that has no intended use or reuse. Contaminated chemicals, chemicals in deteriorating containers, and any other chemical(s) that are no longer used or useful should be considered as a waste.

Federal and state regulations list several categories of substances, which have toxic, carcinogenic, mutagenic, or have teratogenic effects in humans, or have an adverse impact on the environment. These substances are listed by specific sources, non-specific sources, discarded commercial chemical products, container and spill residuals, or are considered acutely or extremely hazardous. Certain substances, which are not specifically listed as a hazardous waste, are still regulated as a hazardous waste because they exhibit one or more of the following characteristics:

Ignitable – A waste exhibits the ignitable characteristic if it is a liquid with a flash point of less than 140° Fahrenheit. This includes solvents such as methanol, ethanol, ethers, and acetonitrile.

Corrosive – A waste exhibits the corrosive characteristic if it is aqueous with a pH less than or equal to 2 or greater than or equal to 12.5.

Reactive – A waste exhibits the reactive characteristic if it is unstable, explosive, water or air reactive, a strong oxidizer, an organic peroxide, or contains cyanide or sulfide bearing materials that release toxic gases in contact with acids.

Toxic – A waste exhibits the characteristic if it contains toxic metals or pesticides; exhibit oral toxicity, contain a known carcinogen or known mutagen; or are toxic to aquatic species.

The Caltech Safety Office picks up hazardous waste from designated places in research groups. The contact person in the Safety Office for this program is Michael Chuah at Caltech extension 6727 or e-mail safety@caltech.edu. Each group's safety officer has designated the place where waste is accumulated and then picked up from. The schedule of waste pick up for each building is available from the Safety Office.

ALL WASTE MUST BE LABELED using tags supplied by the Safety Office.

All hazardous waste that is picked up by the Safety Office must be completely labeled and identified. Principal Investigator's (PI's) and their group members, Facilities personnel, and any other person or entity that produces hazardous waste is responsible for accurately labeling and identifying all wastes under their control. When an unknown waste is discovered, an attempt must be made by the group to identify its contents immediately. In the event that someone cannot identify the waste, than the Institute's hazardous waste contractor will perform an analysis to identify the unknown waste. Any analysis performed by the Institute's hazardous waste contractor will be conducted in the laboratories or location in which it was discovered. The cost of the analysis will be billed back to the appropriate party.

Hazardous wastes should be appropriately segregated. Caution must be exercised in any area where hazardous chemicals or waste are accumulated to be sure that incompatible materials are segregated appropriately. Segregate by the chemical or waste hazard class, not alphabetically. Consult the chemicals Material Safety Data Sheet (MSDS) or any other chemical information resources, such as the Merck Index or Hawley's Chemical Dictionary for compatibility information. The following are examples of incompatible chemicals:

Flammables and Oxidizers;
Elemental Metals and Hydrides;
Cyanides and Acids;
Sulfides and Acids;

Bases and Acids;
Flammables and Acids;
Chlorine Compounds and Acids;
Elemental Metals and Acids;
Chlorine Compounds and Amines;
Air or Water Reactives and Anything;
Organic Peroxides and Anything.

The requirements associated with the hazardous waste tags are:

(1) The container must be tagged when the first drop of hazardous waste goes into it. This is identified on the tag as the “Date Waste is First Generated.”

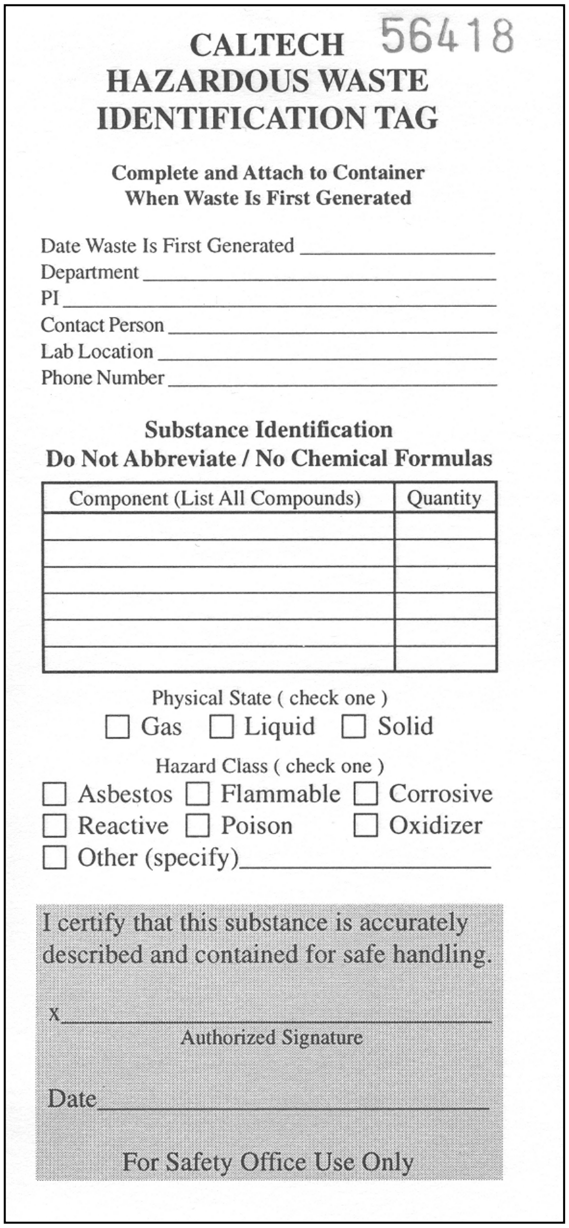
(2) The tag must be completely filled out and dated when the first drop goes into the container.

(3) If your waste container has more chemical compounds than you can list on the tag, then use a continuation sheet in conjunction with the tag. The original tag number on the hazardous waste container must be included on the continuation sheet.

(4) The container must be kept closed unless the transfer of hazardous waste is occurring.

(5) The chemical composition of the waste must be listed on the tag. Formulas and abbreviations are not acceptable for substance identification.

The Caltech Hazardous Waste Identification Tag is as follows. For additional information on filling out the tag, refer to Appendix F: Means of Lab Waste Disposal.



CALTECH 56418
HAZARDOUS WASTE
IDENTIFICATION TAG

Complete and Attach to Container
When Waste Is First Generated

Date Waste Is First Generated ____________________
Department ________________________________
PI ______________________________________
Contact Person ______________________________
Lab Location _______________________________
Phone Number ______________________________

Substance Identification
Do Not Abbreviate / No Chemical Formulas

Component (List All Compounds)	Quantity

Physical State (check one)
☐ Gas ☐ Liquid ☐ Solid

Hazard Class (check one)
☐ Asbestos ☐ Flammable ☐ Corrosive
☐ Reactive ☐ Poison ☐ Oxidizer
☐ Other (specify)____________________

I certify that this substance is accurately described and contained for safe handling.

x________________________________
Authorized Signature

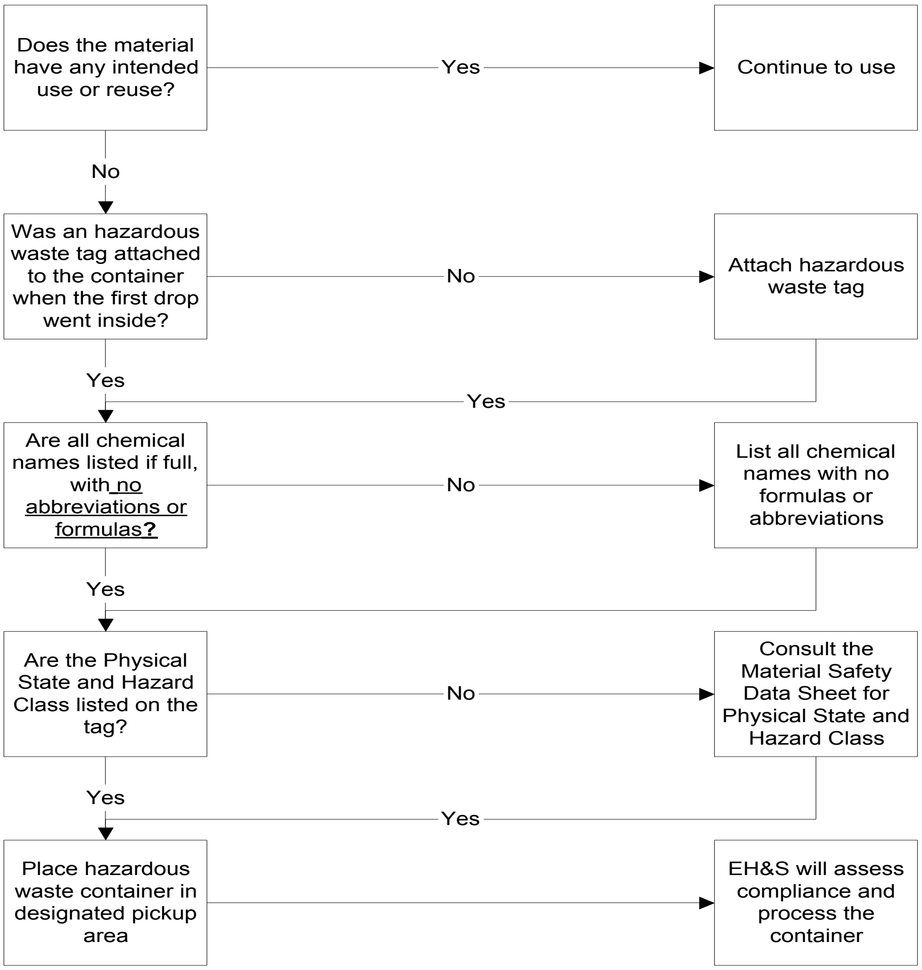
Date________________________________

For Safety Office Use Only

Solvent waste should be accumulated in 5 gallon red plastic containers delivered to labs by the Safety Office when waste is picked up.

An unidentified sample should be deemed hazardous and handled with care.

The following flow chart from the Safety Office manual entitled “Hazardous Waste Management Reference Guide” illustrates the labeling process.



X. Spill Clean up

Attend to any Injuries First.

If there is a **major chemical spill**, immediately alert everyone in the laboratory, confine the contaminated area, and turn off ignition and heat sources. Call the Security Emergency Number at Extension 5000. You should identify yourself, your location and the identity of the spilled material. Have knowledgeable parties assist the emergency personnel. When there is any doubt, a chemical spill is major.

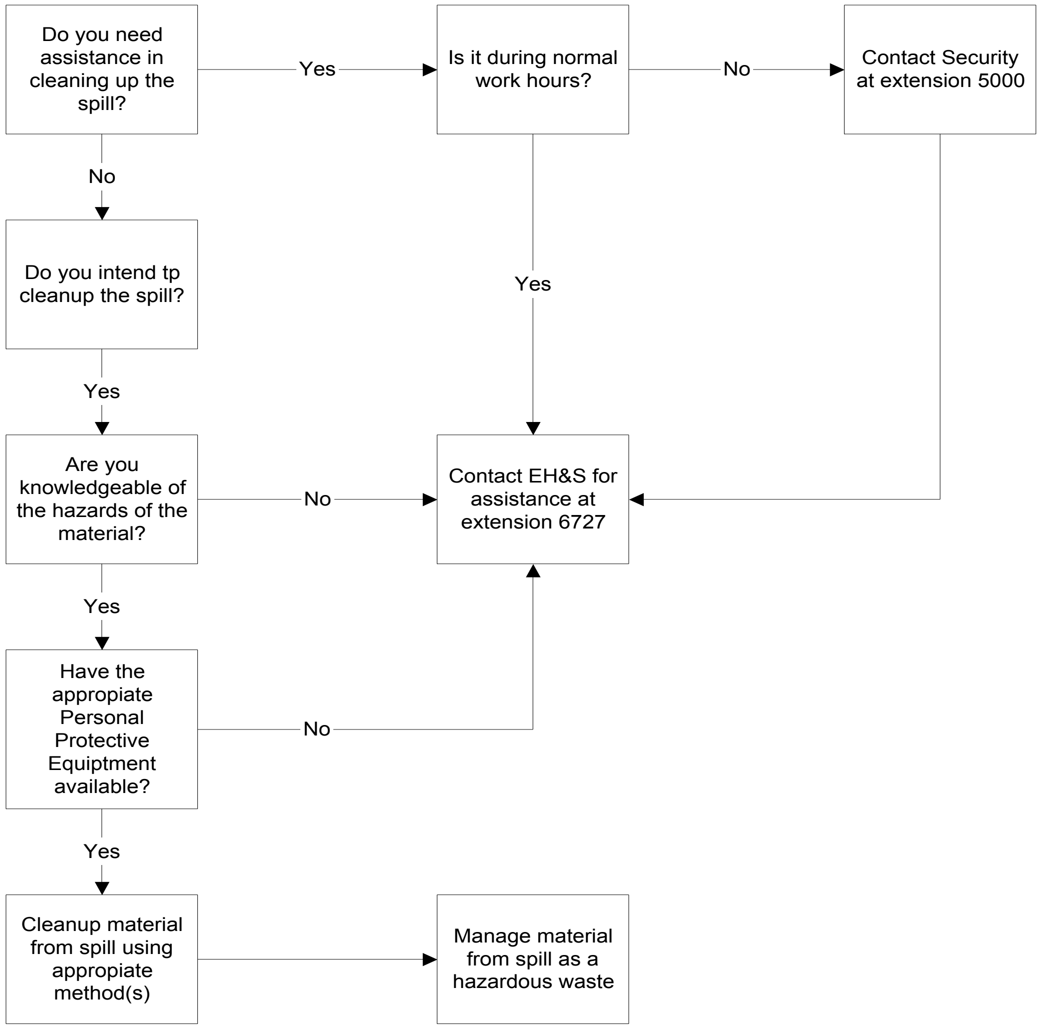
If there is a **minor chemical spill** in the laboratory, immediately alert fellow laboratory workers. When cleaning the spill, wear protective equipment and avoid breathing any vapors from the spill. Use a laboratory spill kit to absorb the spill. Spill kits can be purchased and kept in the labs to permit quick cleanup of spills. Collect all residues from the clean up and treat them as hazardous waste. Clean the area with water after all the chemicals have been collected.

If the **spill is merely water** or some other obviously non-hazardous material, the spill should be cleaned up by the researcher. Although the Facilities Manager may have access to the custodial closets it is advisable for each group to have its own mop, bucket and broom. These items can be obtained from Physical Plant for a small charge. This practice minimizes the time something remains on the floor while the person is looking for someone with a key to the custodial closet.

The following flow charts from the Safety Office manual entitled “Hazardous Waste Management Reference Guide” illustrate how to handle a small spill and a large spill.

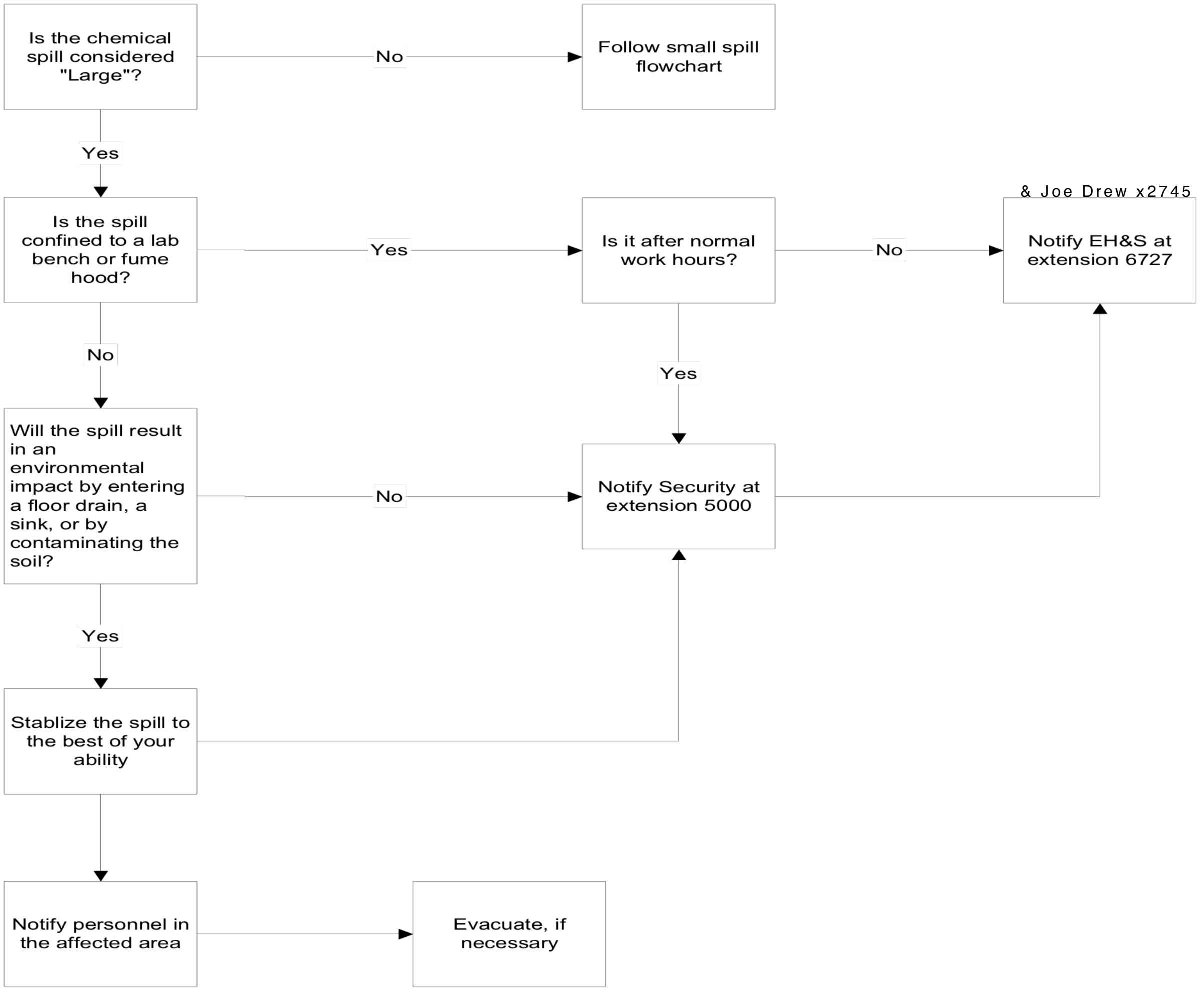
Handling a small spill.

The following flow chart illustrates the steps to take in the event of a small spill. If there is any uncertainty whether the spill is manageable, contact the Safety Office or Security immediately.



Handling a large spill.

In the event that a spill is large, not contained, or has a potential environmental impact, Security and/or the Safety Office must be notified immediately. In addition, personnel will do the following:



For additional information, refer to the Caltech Emergency Response Guides posted in each laboratory.

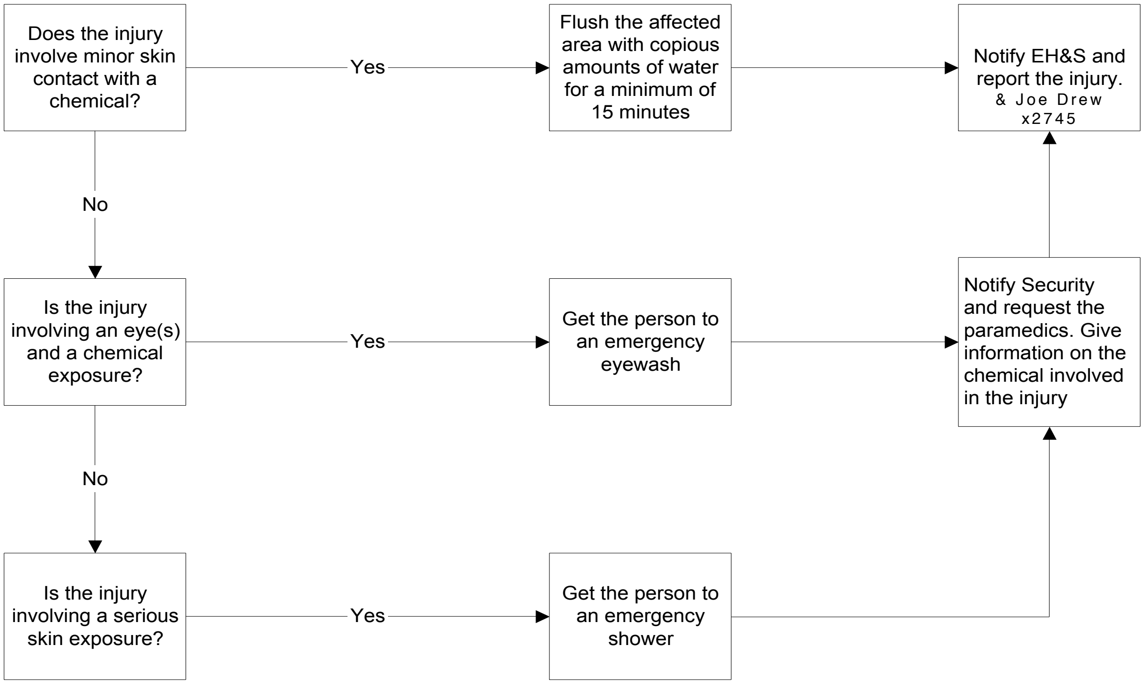
XI. Responding to an Incident

Consult the Caltech Emergency Response Guide, which is a compilation of information on how to respond to various emergencies. These guides are posted in laboratories and other strategic locations.

For emergencies involving fire, explosion or health threatening incidents, the following apply:

Call Security at ext. 5000 for emergency assistance
Alert people in the area of the incident
Evacuate the area (if necessary)
Provide information to emergency personnel. Provide only information that is accurate and essential for emergency personnel to make a correct judgment about their response. Do not embellish or speculate.

For injuries involving a chemical, you may use the following flow chart from the Safety Office manual entitled "Hazardous Waste Management Reference Guide" to determine a course of action.



XII. Safety Consideration in Work Planning

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.

(A) Recognition and Assessment

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

Some of the important factors that must be considered include:

Physical Properties

- Vapor pressure?
- Boiling point?
- Flash point?
- Auto-ignition temperature? At what pressure?
- Explosion limits in air? At what temperature?
- Are the materials and quantities such that **Prestart-Up Inspection** or Reactive Chemist Review is required? (For Prestart-Up Inspection triggers and procedure see page **32**)

Chemical Reactivity

- Will it form peroxides?
- Is it a strong oxidizing or reducing agent?
- Will it react violently with water? Will it decompose spontaneously?
- How is it affected by heat, light, pressure, etc.?

Will it react exothermically with any other types of material?
How much potential energy is stored in this molecule?
Are the materials and quantities such that Prestart-Up review is required?

Health Effects

Is it corrosive, an irritant, a sensitizer?
Is it carcinogenic? mutagenic? teratogenic? a biohazard?
Does it have any acute or chronic toxic properties?
Is it regulated by any government agencies?
Are there established permissible exposure limits?
Are the materials and quantities such that Prestart-Up Inspection or Reactive Chemicals Review is required?
Is radiation (ionizing or non-ionizing) present or of concern?

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

Are there any potentially incompatible materials?
What is the heat of reaction?
Could any undesirable byproducts be formed?
How much energy would be released?
Are there any health hazards?
Is the material's composition certain?
What are the consequences of inadequate mixing?

(B) What Could Happen?

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?
Feed pump fails?
Seals fail?
Agitation is lost?
Too much of a reactant added?
A spill occurs?
Etc.

(C) 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.

XIII. Group Safety Plans

Each research group will have a safety plan that covers the special hazards that are associated with their research. Safety issues will be a regular topic in group meetings to update the safety plan and to maintain the researchers' awareness of safety topics and procedures.

XIV. General Laboratory Safety Inspection

General laboratory safety inspections are the responsibility of the Institute Safety Office. These inspections focus on OSHA standards and other general safety features.

These inspections are conducted annually by representatives of the Institute Safety Office, the Division Environment, Health & Safety Liaison, and the Laboratory Safety Officer. Areas to be covered are:

Inspection of lab

Hood performance
Fire and earthquake hazards
Gas tank security
Safety documentation
Solvent storage
General housekeeping of the lab

Follow up

reports
variance documents

The Caltech Safety Liaison will report fume hood deficiencies to the researcher and directly to Physical Plant for correction. Other items requiring attention by Physical Plant, such as installation of gas cylinder racks and straps for equipment on lab benches, will be reported to the researcher involved, the faculty supervisor, and the CCE Safety Liaison, who will be jointly responsible for the correction of the problem. The faculty supervisor and group safety officer will be notified of other matters requiring research group attention and for which the faculty supervisor and safety officer are responsible to rectify such as housekeeping, secondary containment, and other specialized matters. The CCE Division Safety Committee will evaluate any new or changed safety policies and practices for the CCE Division.

XV. Prestart-Up Inspection/Reactive Chemicals Program

The first step in a Reactive Chemicals Program is to learn the hazards associated with a chemical or a process. It is the responsibility of each researcher to obtain the proper information needed to characterize the reactive chemical hazards of the material or process. Existing information may be obtained from the sources posted in the laboratory and in the Appendix to this manual. The Reactive Chemicals Index contains information on any previous reactive chemicals evaluation of a material. New chemicals should be considered to fall into the most dangerous categories until proven otherwise.

When the appropriate reactive chemicals data have been obtained, the complete experiment or process must be evaluated as to scale and danger.

Small-scale laboratory experiments that do not involve significant quantities (see triggers for prestart-up inspection) of material (or will not involve materials or mixtures with significant potential for energy release) may be evaluated and approved for start-up by the individual researcher.

Review appropriate material to determine if any materials or chemicals in the intended operation are regulated by federal or state law.

Undergrads, temporary researchers, or researchers without the technical training to evaluate potential hazards must consult with their supervisor before starting an experiment.

(A) What is a Local Prestart-Up Inspection?

The Prestart-Up Inspection is a protocol for evaluating the risks of a new procedure, drawing on the experience of other researchers, and ensuring that all safety factors have been considered. The following sections describe what triggers a Prestart-Up Inspection and how to perform it.

(B) When to Initiate a Prestart-Up Inspection

Fundamentally, a Prestart-Up Inspection should be undertaken whenever a new procedure is attempted even if the procedure seems to be fully described in the literature. A Prestart-Up Inspection should be conducted whenever there is any question as to the safety of an experiment or process.

A prestart-up inspection *must be* held when the new experiment or process involves handling any of the following: (*stills, rotovaps, vac lines, etc. only require initial inspection)*

- Pressures > ± 1 atm psig glass; > 100 psi in custom metal apparatus
- Volumes > 3 liters
- A continuous process (stills etc.)
- > 500 ml of a red 3 or 4 flammable material
- > 1 liter of red 2 flammable material
- > 0.1 gram mole of yellow 4 reactive material
- > 0.5 gram mole of a yellow 3 or 4 reactive material
- > 0.1 gram mole of a blue 4 toxic material
- > 50 ml or > 50 g of any blue 3 toxic material
- Regulated chemicals. These materials have identified human health hazards that often require concentration monitoring or further personal protective equipment beyond the protection provided by lab hoods, safety glasses, goggles, gloves, or lab coats.
- Recombinant DNA (rDNA) operations require review for compliance with National Institutes of Health (NIH) guidelines. Contact the Division Safety Coordinator or Safety Office for details.

- Some biological agents due to their particular virulence, pathogenicity, route of spread, biological stability, endemicity and communicability, quantity and concentration, procedures involved, and availability of effective vaccines or therapeutic measures require additional safety precautions in accordance with NIH guidelines and California State regulations. These agents may be of moderate risk but may carry more serious or lethal consequences. They often require biological safety cabinets, written procedures, and restricted access to the laboratory. Blood borne pathogens are pathogenic organisms in the blood, most notably hepatitis B and HIV. Contact the Safety Office for assistance.

- Use of radioactive material requires review and approval by the Radiation Safety Committee. Similarly, initial set-up of radiation-producing equipment must be inspected by Radiation Safety and approved by the Radiation Safety Committee. Contact the Division Safety Coordinator (Joe Drew).

- Non-ionizing radiation-producing equipment such as lasers, microwaves, ultra-violet light may require inspection prior to use. Contact the Safety Office for assistance.

These above constitute minimum requirements. Even when a prestart-up inspection is not required, line supervision must be informed when red labeled toxic material use is intended.

(C) How to Conduct a Prestart-Up Inspection

A laboratory level prestart-up inspection committee consisting of the researcher or researchers involved, the group safety officer, and any other qualified personnel appointed by the laboratory director, may conduct a prestart-up inspection upon the request of a researcher or research supervisor. The inspection committee is advisory to the supervisor. Each laboratory or area must have a written prestart-up form and procedure stating the subjects that must be covered. As a minimum, the approval and signature of the safety officer is required for start-up authorization.

A form to be used for prestart-up inspections is included as Appendix M. The completed document will be posted near the experiment. At the conclusion of the experiment, the document will be kept on file by the group safety officer for future reference. The location of the file will be made known to all group members, the faculty supervisor, and the Caltech Safety Office.

Prestart-up inspection must cover at a minimum:

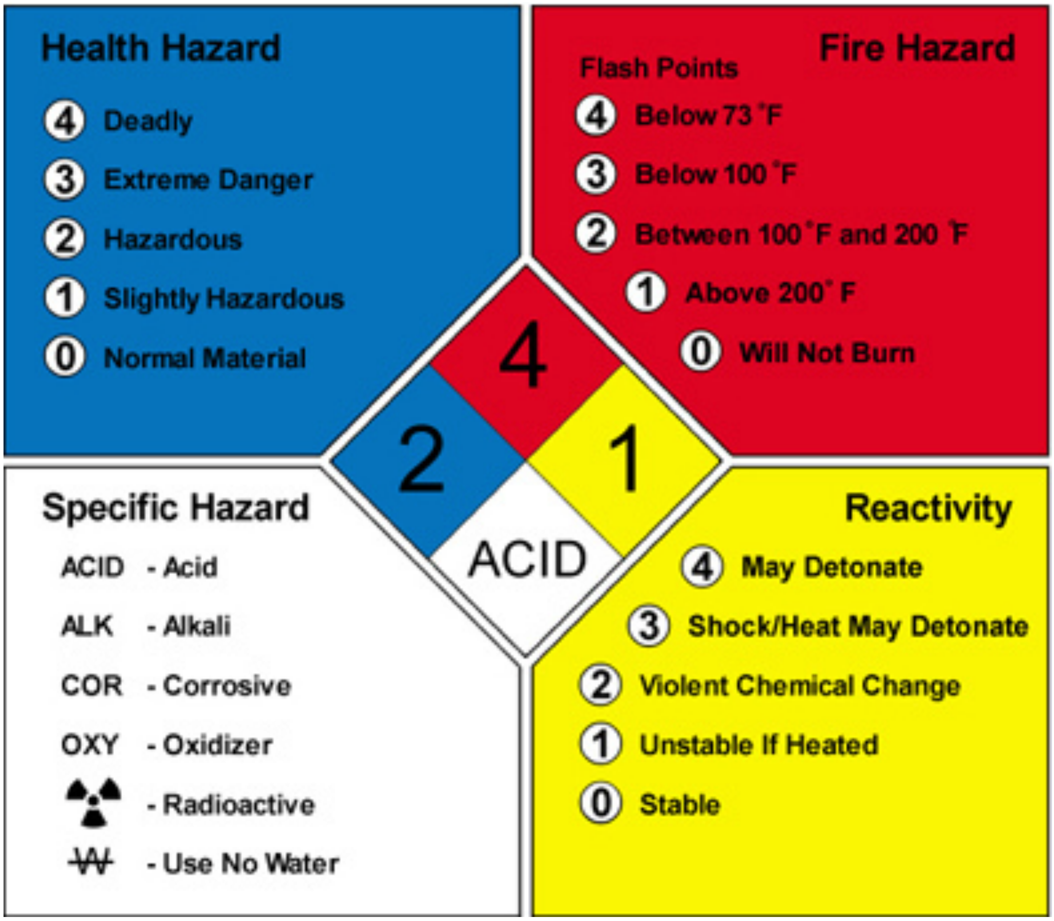
- A review of the reactive chemical potential of the material or process.
- A review of the potential health hazards of the material or process, as well as procedures to be followed in manipulating the materials.
- An inspection and review of the reaction site and all associated equipment, reactors, operating procedures, waste disposal procedures, chemical storage areas, and safety procedures, equipment, etc.

Each member of the inspection committee must consider the question: "What is the worst possible event or series of events that could occur?" The committee must agree that to the best of their knowledge no injury or significant damage could occur under the worst possible set of circumstances.

It is the responsibility of the researcher to provide the necessary data and hazard interpretation associated with the experiment or process. It is the **responsibility of the supervisor** to verify that the appropriate testing and evaluation has occurred and to **authorize start-up** of the operation. The supervisor, who retains ultimate responsibility, may delegate the safety officer to authorize start-ups.

XVI. Hazard Identification Diagram

The code is from the National Fire Prevention (NFP) Code. The first number relates to Health (blue) Hazards, the second number relates to Flammability (red), and the third to Reactivity (yellow). The number designation is taken from the manual of NFP.



Health (BLUE)

4 A few whiffs of the gas or vapor could cause death or the gas, vapor, or liquid could be fatal on penetrating the fire fighter's normal full protective clothing which is designed for resistance to heat. For most chemicals having a Health 4 rating, the normal full protective clothing available to the average fire department will not provide adequate protection against skin contact with these materials. Only special protective clothing designed to protect against the specific hazard should be worn.

3 Materials extremely hazardous to health, but areas may be entered with extreme care. Full protective clothing, including self-contained breathing apparatus, rubber gloves, boots and bands around legs, arms and waist should be provided. No skin surface should be exposed.

2 Materials hazardous to health, but areas may be entered freely with self-contained breathing apparatus.

1 Materials only slightly hazardous to health. It may be desirable to wear self-contained breathing apparatus.

0 Materials which on exposure under fire conditions would offer no health hazard beyond that of ordinary combustible material.

Flammability (RED)

4 Very flammable gases, very volatile flammable liquids, and materials that in the form of dusts or mists readily form explosive mixtures when dispersed in air. Shut off flow of gas or liquid and keep cooling water streams on exposed tanks or containers. Use water spray carefully in the vicinity of dusts so as not to create dust clouds.

3 Liquids which can be ignited under almost all normal temperature conditions. Water may be ineffective on these liquids because of their low flash points. Solids which form coarse dusts, solids in shredded or fibrous form that create flash fires, solids that burn rapidly, usually because they contain their own oxygen, and any materials that ignite spontaneously at normal temperatures in air.

2 Liquids which must be moderately heated before ignition will occur and solids that readily give off flammable vapors. Water spray may be used to extinguish the fire because the material can be cooled to below its flash point.

1 Materials that must be preheated before ignition can occur. Water may cause frothing of liquids with this flammability rating number if it gets below the surface of the liquid and turns to steam. However, water spray gently applied to the surface will cause a frothing which will extinguish the fire. Most combustible solids have a flammability rating of 1.

0 Materials that will not burn.

Reactivity (YELLOW)

4 Materials which in themselves are readily capable of detonation or of explosive decomposition or explosive reaction at normal temperatures and pressures. Includes materials which are sensitive to mechanical or localized thermal shock. If a chemical with this hazard rating is in an advanced or massive fire, the area should be evacuated.

3 Materials which in themselves are capable of detonation or of explosive decomposition or of explosive reaction but which require a strong initiating source or which must be heated under confinement before initiation. Includes materials which are sensitive to thermal or mechanical shock at elevated temperatures and pressures or which react explosively with water without requiring heat or confinement. Fire fighting should be done from an explosion-resistant location.

2 Materials which in themselves are normally unstable and readily undergo violent chemical change but do not detonate. Includes materials which can undergo chemical change with rapid release of energy at normal temperatures and pressures or which can undergo violent chemical change at elevated temperatures and pressures. Also includes those materials which may react violently with water or which may form potentially explosive mixtures with water. In advanced or massive fires, fire fighting should be done from a protected location.

1 Materials which in themselves are normally stable but which may become unstable at elevated temperatures and pressures or which may react with water with some release of energy but not violently. Caution must be used in approaching the fires and applying water.

0 Materials which are normally stable even under fire exposure conditions and which are not reactive with water. Normal fire fighting procedures may be used.

Appendix A lists the NFPA data for common chemicals. Many chemicals now arrive with NFPA data on the label.

XVII. Health Hazards of Chemicals – Use Requirements for Toxic and Regulated Chemicals

Many chemicals have health hazards that are known through extensive testing, laboratory investigation, occupational experience or by other means. For some chemicals, use is regulated by federal and state law. It is the responsibility of the researcher to handle with appropriate industrial hygiene all aspects of chemical manipulation.

The researcher must treat all chemicals of unknown toxicity as though they present a health hazard. Remember that some materials have a delayed effect or do not have any warning activity, while others can be detected by odor but only at levels that are already hazardous. When working with toxic materials, there is no substitute for "Knowing Your Chemicals", good planning, and a well-designed apparatus in an appropriate location.

Know beforehand the location of the nearest eyewash fountain, sink, and safety shower. Know what to do in an emergency before it occurs.

Consistent with Caltech Policy, Caltech will provide medical consultation, medical examinations, and any necessary follow-up examinations to laboratory employees under the following circumstances: (a) whenever an employee develops signs or symptoms associated with a hazardous chemical to which the employee may have been exposed in the workplace; (b) whenever a spill, leak, explosion or other occurrence takes place which results in the likelihood of a hazardous exposure; (c) when exposure monitoring reveals an exposure level routinely above the Action (or Exposure, if no Action Level exists) Level specified by OSHA regulations, for a chemical that has medical surveillance requirements in the OSHA regulations.

All personnel with concerns regarding reproductive toxins present or suspected in the work environment must contact the Safety Department at extension 6727.

(A) The Main Health Hazards:

1. Eye Exposure

If a chemical comes in contact with the eyes, avoid rubbing but immediately and thoroughly wash the eyes with flowing water in the nearest eye wash fountain – **SPEED IS ESSENTIAL**. Have someone dial and summon emergency help. Continue washing for 15 minutes or until the ambulance arrives. It is not good practice to wear contact lenses in the laboratory.

2. Skin Exposure

A prudent laboratory practice is to avoid ALL skin contact with laboratory chemicals. If skin exposure occurs, wash the entire exposed area thoroughly with water – **SPEED IS ESSENTIAL**. For some small area exposures, a sink faucet may be the closest water source and completely suitable to wash the area, however, do not hesitate to use the nearest safety shower if the exposure area cannot be completely covered by water from a sink faucet.

3. Inhalation Exposure

Work in a chemical fume hood to lessen inhalation of potential vapors and dust. If illness from inhalation of a chemical occurs, remove the person at once to fresh air, keep quiet and warm. Dial 5000 to summon an ambulance. If breathing has stopped, begin artificial respiration at once.

Since most chemical fume hoods vent above the roof, be aware of and inform the Division Safety Coordinator or Division Administrator if toxic or noxious chemicals may be released by the laboratory operation. Do not endanger people working outside the building or on the roof by hood activities.

4. Ingestion

Wash hands before eating. Do not use laboratory glassware for eating or drinking. These precautions are especially important for anyone working with highly toxic chemicals, microorganisms, parasites or radioactive materials.

(B) Handling Requirements for Highly Toxic Materials:

A Prestart-Up Inspection is mandatory when > 250 ml or > 250 grams of Blue 3 or 4 (danger category) toxic chemical is proposed for laboratory operation. Prestart-Up Inspection may be requested whenever a review of proposed laboratory operation and work practices is appropriate as judged by the researcher , faculty supervisor or Group Safety Officer.

Fellow workers in the area must be informed of the nature of the toxic material and the hazards involved.

Toxic materials are normally handled in an effective hood which must be checked or known to be capable of containing vapors and airborne particles. Hoods must be considered as safety devices in case of accidental release and not as disposal units. Use of scrubbers or other means of trapping gaseous effluent from reactions is required. Most hoods exhaust contaminated air directly to the roof of the building. There have been many instances of contamination of the work area from exhaust air being readmitted to the building through intake by the "fresh air" handling system. For consultation and recommendations on the handling of materials to avoid chemical exposure, consult the Safety Office, Safety Officer, or other technically qualified individuals.

(C) Select Carcinogens

1. These "select carcinogens", reproductive toxins, and substances have a high degree of acute toxicity. *The presence or suspected presence of any chemical found in the following listings REQUIRES contact with the Safety*

Office to obtain additional information about proper use and disposal of this material.

"Select carcinogens" are defined as those substances that meet one or more of the following criteria:

(a) It is regulated by OSHA as a carcinogen

(b) It is listed under the category" known to be carcinogens" in the Annual Report on Carcinogens published by the National Toxicology Program (NTP) (latest edition); or

(c) It is listed under Group 1 ["carcinogenic to humans"] by the International Agency for Research on Cancer Monographs (IARC) (latest editions) or;

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

  [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, or

  [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.

2. CAL/OSHA-Regulated Carcinogens or Potential Carcinogens

Compounds that meet criterion (C.1.a) are listed below:

- 2-acetylaminofluorene
- 3,3'-dichlorobenzidine and its salts
- 4-aminodiphenyl
- 4-dimethylaminoazobenzene
- 4-nitrosodimethylamine
- 1,2-dibromo-3-chloropropane (DBCP)
- a-naphthylamine (1-naphthylamine)
- acrylonitrile
- arsenic compounds (inorganic)
- asbestos
- beta-naphthylamine (2-naphthylamine)
- 4-nitrobiphenyl
- 4,4’-methylenebis(2-chloroaniline) (MBOCA)
- b-propiolactone
- benzene
- benzidine and its salts
- 1,3 butadiene
- bis-chloromethyl ether
- coal tar pitch volatiles
- coke oven emissions
- ethylene oxide (EtO)
- ethyleneimine
- ethyle dibromide (EDB)
- formaldehyde
- methyl chloromethyl ether
- N-nitrosodimethylamine
- methylene chloride
- methylenedianiline (MDA)
- cadmium
- vinyl chloride

3. NTP: Substance Known to be Carcinogenic

Compounds which meet criterion (C.1.b) are:

- 2-naphthylamine (b-naphthylamine)
- 4-aminobiphenyl
- 1,4-butanediol dimethanesulphonate
- cobalt-chromium alloy
- amosite
- anthophyllite
- arsenic and certain arsenic compounds

arsenic trioxide
arsenic, inorganic compounds
asbestos
asbestos, crocidolite
azathioprine
benzene
benzidine
bis(chloromethyl ether)
calcium chromate, sintered
chloramethyl methyl ether, technical grade
chromic acid, calcium salt (1:1)
chromium and certain chromium compounds
chromium trioxide, including sintered material
chrysolite
coke oven emissions (polycyclic organic matter (POM))
cummingtonite-grunerite
diethylstilbestrol
estrogens, conjugated
lead chromate
lead chromate (IV) oxide
melphalen
methoxsalen with ultraviolet A therapy (PUVA)
mustard gas (phosgene)
phenacetin, analgesic mixtures containing
radon
soots, tars and mineral oils
strontium chromate
thorium dioxide
tremolite
vinyl chloride
zinc chromate

*this list current as 11/1/2013

4. IARC Group 1 Carcinogens:

Compounds that meet criterion (C.1.c) are:

- 2-naphthylamine (b-naphthylamine)
- 4-aminobiphenyl
- aflatoxins
- arsenic and certain arsenic compounds
- asbestos
- azathioprine
- benzene
- benzidine
- bis(chloromethyl) ether (BCME)
    - chloromethyl methyl ether (tech. grade)
    - chromium compounds, hexavalent
    - coal tar pitches

cyclophospharmide
erionite
mustard gas [1,1'-thiobis(2-chloro-ethane)]
nickel and certain nickel compounds
soots
tobacco smoke
talc containing asbestiform fibers
vinyl chloride

5. Selected compounds of concern that meet criterion (C.1.d) are:

1-Amino-2-methylanthraquinone
1,1'-Dimethylhydrazine
1,2'-Dimethylhydrazine
2-Methyl-1-nitroanthraquinone (uncertain purity)
4,4'-Diaminodiphenyl (oxydianiline)
4,4'-Thiodianiline
4,4'-Methylene bis(2-methylaniline)
1,3-Dichloropropene
2,4-Diaminoanisole
2,4-Diaminotoluene
3,3-Dimethoxybenzidine (o-Dianisidine)
4,4-Methylene dianiline
2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD)
a-Chlorinated toluenes
Acrylamide
Benzotrichloride
Cadmium and compounds
Carbon tetrachloride
Chlorendic acid
Crystalline silica
Diglycidyl resorcinol ether
Epichlorohydrin
Ethylene dibromide
Ethylene thiourea
Hexachlorobenzene
Hexachlorocyclohexanes
Hexamethylphosphoramide
Hydrazine
Hydrazobenzene
Lead and lead compounds, inorganic
Methyl methanesulphonate
Methylaziridine
Methylazoxymethanol and its acetate

  - Michler's ketone
  - N,N'-Diacetylbenzidine
  - o-Aminoazotoluene
  - p-Aminoazobenzene
  - p-Cresidene
  - p-Dimethylaminoazobenzene
- Phenazopyridine hydrochloride
- Polybrominated biphenyls (PBBs)
- Polychlorinated biphenyls (PCBs)
- Potassium bromate
- Selenium sulfide
- Thioacetamide
- Thiourea
- Tris (2,3-dibromopropyl) phosphate
- Urethane

6. Nitrosamines or Polycyclic Compounds That Appear on IARC 2A or 2B or NTP "Anticipated" Carcinogens Lists

There has been no effort to categorize the relatively large number of nitrosamines and polycyclic compounds that are found in the NTP and IARC lists. Personnel working with nitrosamines, polynuclear aromatics, or polynuclear heterocyclic compounds must refer to the list, found below, of those compounds in these chemical families that are listed in IARC 2A or 2B categories or by NTP as "reasonably anticipated to be carcinogens". These materials are listed in the following table.

COMPOUND	IARC Listing 2A	IARC Listing 2B	NTP Antic.
Nitroso-Compounds			
bischloroethyl nitrosourea	X		X
1-(2-chloroethyl)-3-cyclohexyl-1-nitrosourea	X		X
N-methyl-n-nitrosourea	X		
N-methyl-N-nitrosourea	X		
N-methyl-N-nitrosourethane		X	
N-nitrosodi-n-butylamine		X	X
N-nitrosodiethanolamine		X	X
N-nitrosodiethylamine	X		X
N-nitrosodimethylamine	X		X
p-nitrosodiphenylamine			X
N-nitrosodi-n-propylamine		X	X
N-nitroso-N-ethylurea			X
3-(N-nitrosomethylamino)propionitrile		X	
N-Nitroso-N-methylurea			X
N-nitrosomethylvinylamine		X	X
N-nitrosomorpholine		X	X
N-nitrosonornicotine		X	X
N-nitrosopiperidine		X	X
N-nitrosopyrrolidine		X	X
N-nitrososarcosine			X

COMPOUND	**IARC**	**Listing**	**NTP**
	2A	**2B**	**Antic.**
benz[b]fluoranthene		X	X
benzo[j]fluoranthene		X	X
benzo[k]fluoranthene		X	X
benzo[a]pyrene	X		X
dibenz[a,h]acridine		X	X
dibenz[a,j]acridine		X	X
dibenz[a,h]anthracene	X		X
7H-dibenzo[c,g]carbazole		X	X
dibenzo[a,e]pyrene		X	X
dibenzo[a,h]pyrene		X	X
dibenzo[a,j]pyrene		X	X
dibenzo[a,l]pyrene		X	X
indenol[1,2,3-cd]pyrene		X	X
5-methylchrysene		X	X

In addition, there are compounds that are classified either Group 2A or 2B by IARC or under the category "reasonably anticipated to be carcinogens" by NTP, and have shown carcinogenic properties at all doses tested, but whose lowest dose tested *exceeds* the value indicated by OSHA in the definition cited above. These compounds are:

Acetaldehyde
Acetamide
2-Aminoanthraquinone
o-Anisidine and hydrochloride
1,3-Butadiene
g-Butyrolactone

Chlorinated paraffins
3-Chloro-2-methylpropene
4-Chloro-o-phenylenediamine
p-Chloro-o-toluidine
Cupferron
Diepoxybutane
Di(2-ethylhexyl)phthalate
Dimethyl sulfate
Dimethylvinyl chloride
Ethyl acrylate
Glycidaldehyde
4,4-'Methylenebis (2-chloroaniline) (MBOCA)
5-Nitro-o-anisidine
2-Nitropropane
Styrene oxide
o-Toluidine
2,4,6-Trichlorophenol
Vinyl bromide

Finally, there are compounds that also have either the IARC 2A or 2B classification or the NTP "reasonably anticipated" designation for which insufficient date exist to make a judgment on whether or not they fall into the "Select Carcinogen" category. These compounds include:

Beryllium
Diethyl sulfate
Pentachlorophenol
3,3'-Dichloro-4,4'-diaminodiphenyl ether
1,2-Diethylhadrazine
3,3-Dimethylbenzidine (o-Toluidine)
Ethyl methanesulfonate
Phenoxybenzamine HCl
2,4,5-Trichlorophenol

XVIII. Information Sources for Hazard Evaluation

(A) For Known Properties of Chemicals

1. Vendor Material Safety Data Sheets (MSDS) – Each vendor must provide a MSDS for chemicals sold. These sheets can be a valuable source of information. Contact the assistant to the Safety Office for a copy. MSDS are also available on the internet at www.hazard.com.

2. National Fire Codes (1979) – Published by the National Fire Protection Association (NFPA). This manual set has a great deal of information on the flammability and reactivity properties of common industrial chemicals. Sections **325A and 325M** contain tables of flash point and boiling point data.

3. Registry of Toxic Effects of Chemical Substances (RTECS) – This compilation of known toxicological data is updated frequently. Most libraries maintain a copy. A more current copy of the RTECS can be accessed by contacting the Institute Safety Office.

In addition, many libraries contain books covering safety and hazard identification.

(B) Obtaining Information on New Materials

When specific hazard information on a new material or a material for which no data exist is required, the requisite testing may be obtained through:

1. Outside Testing Firms (Safety Office)

   Tests needed to determine the flammability and reactivity hazards of a chemical include:

   Dust explosion hazard

Flash point and flammability limits
Shock sensitivity
Thermal stability
Thermodynamic calculation of potential energy

Many of these tests are required as a part of a prestart-up inspection or reactive chemicals review.

2. Health and Environmental Sciences Toxicology Testing

Data on the health hazards of a chemical or mixture of chemicals such as toxicity, skin sensitivity, etc. can be obtained by contacting the chemical hygienist.

If unknown chemicals are to be used on a large scale, testing for health hazards should be made by outside firms. All new materials should be treated as dangerous until shown otherwise by testing.

XIX. Peroxide-Forming Compounds

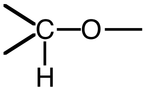
Peroxide formation in laboratory solvents and reagents has been the cause of many laboratory accidents. Be aware of the potential hazard and plan accordingly.

The degree of danger from peroxide presence varies considerably. In general, pure compounds are more susceptible to peroxide build up. The more volatile the compound, the greater its potential hazard since, on evaporation, concentration of the peroxide product can more readily occur. It must be *recognized* that *each system* presents its *own structure*.

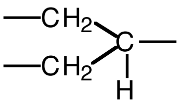
(A) Structure of Peroxide-Forming Compounds

Whenever a compound contains one of the following organic structures, it is a potential peroxide former and often is a potential hazard. It is important for laboratory personnel to recognize these peroxide forming chemical structures. (Figure from *Handbook of Reactive Chemical Hazards, 3rd edition*, L. Bretherick, Butterworths, 1985, p. S-22.)

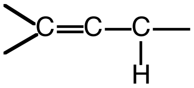
Structures relevant to PEROXIDISABLE COMPOUNDS



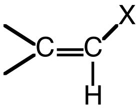
as in acetals, ethers, oxygen heterocycles



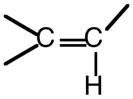
as in isopropyl compounds, decahydronaphthalenes



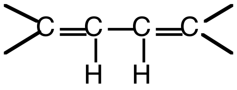
as in allyl compounds



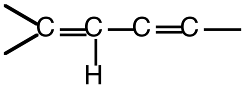
as in haloalkenes



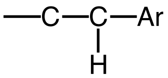
as in other vinyl compounds (monomeric esters, ethers, etc.)



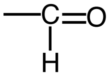
as in dienes



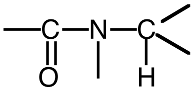
as in vinylacetylenes



as in cumenes, tetrahydronaphthalenes, styrenes



as in aldehydes



as in *N*-alkyl-amides or -urens, lactams

(B) Examples of Peroxide-Forming Compounds

1. List A

Compounds that form explosive peroxide compositions even without concentration. Each of the compounds listed has been a killer. Storage after opening shall be limited to three months. Before disposal of any List A material, the properties and volume of the material must be reviewed with the safety coordinator to insure a safe method of disposal.

Divinyl acetylene
Isopropyl ether
Potassium metal
Sodium amide
Vinylidene chloride

2. List B

These are materials forming peroxides hazardous only on concentration by distillation, evaporation, etc. List B chemicals must not be stored longer than *three or twelve months* after opening (see table).

Three months	**Twelve months**
Diethyl ether	Methylacetylene Acetal
Tetrahydrofuran Dioxane	Decahydronaphthalene Glyme
Dicyclopentadiene Dioxane	Tetrahydronaphthalene Diglyme
Diacetylene Tetrahydrofuran	Cyclohexene Vinyl ethers

3. List C

The compounds listed below are examples of vinyl monomers that form peroxides, which by themselves may not be particularly hazardous, but which, on decomposition, *may initiate explosive polymerization* of the bulk monomer. Storage after opening must be limited to *12 months*.

Acrylic Acid
Acrylonitrile
Butadiene*
Chloroprene
Chlorotrifluoroethylene
Methyl methacrylate
Styrene
Tetrafluoroethylene
Vinyl acetate
Vinyl acetylene
Vinyl chloride
Vinyl pyridine
Vinylidene chloride*
*particularly dangerous

(C) Ordering and Storage of Peroxide-Forming Materials

It is recommended that peroxide-forming materials be purchased in packaged units limited to a maximum of one liter, and that the unit ordered should correspond to the amount needed in an experiment or short series of experiments. The unused portion of the opened material is discarded at the completion of the experiment or not later than the end of the approved storage period for that chemical. *All peroxide-forming chemicals must be dated when received and when first opened.* When a peroxide-forming material must be retained for a longer storage period after opening than the mandated storage time, then the material must be tested and shown to be free of peroxides; the peroxide-free material then is redated to establish a new storage period. All peroxide-forming compounds must be *tightly sealed* to prevent evaporation, and stored away from heat and light.

(D) Handling Precautions

It is recommended that, as a precautionary measure, any peroxide-forming material be tested for peroxide before use. If positive, discard the material or remove the peroxide by an appropriate chemical reaction.

Before distilling any List C Material, a suitable polymerization inhibitor must be added. Leave at 10% residue when distilling peroxide-forming compounds. Most accidents involve a nearly dry residue.

Use a shield when concentrating, evaporating or distilling mixtures that may contain peroxide-forming compounds. Use a boiling aid or magnetic stirrer in preference to a nitrogen bleed to maintain ebullition. Never employ an air purge. Rotary evaporators can be hazardous when operated under reduced pressure to concentrate peroxide-forming materials. Concentration of a dioxane solution in a laboratory rotary evaporator may result in an explosion when disconnecting the main flask. The peroxide formed in the glass joint. In the case of higher boiling peroxidizable compounds such as diglyme or triglyme, any peroxides formed are ordinarily decomposed thermally by the heat required for distillation at atmospheric pressure. However, when such higher boiling peroxidizable compounds are distilled at reduced pressure, the boiling temperature, may be lower than the decomposition temperature and concentration to a hazardous explosive mixture can result.

(E) Detection of Peroxides

Curtis Matheson Sci., Inc. offers a peroxide test kit for the semiquantitative determination of peroxides.

XX. Oxidizing Agents, Explosives and Shock Sensitive Materials

(A) Oxidizing Agents

Air is the prime example of an oxidizing agent. Many other materials will oxidize even in the absence of air or gaseous oxygen. It must not be assumed that heat is required to initiate oxidation.

The following classes of compounds are noted for their ability to oxidize:

Perchlorates	$NaClO_4$, $KClO_4$, NH_4ClO_4, $Cu(ClO_4)_2$, $Mg(ClO_4)_2$
Chlorates	$NaClO_3$, $KClO_3$, etc.
Chlorites	$NaClO_2$, $KClO_2$
Hypochlorites	NaClO, KClO, etc.
Bromates	$NaBrO_3$, $KBrO_3$, etc.
Iodates	KIO_3
Nitrates	NH_4NO_3, KNO_3, $Cu(NO_3)_2$, etc.
Nitrites	NH_4NO_2, KNO_2, $NaNO_2$
Nitrogen Tetroxide	N_2O_4
Chromates	K_2CrO_4, $(NH_4)_2Cr_2O_7$, etc.
Ozone	O_3
Manganates	K_2MnO_4, $CuMnO_4$
Periodates	$NaIO_4$, KIO_4
Permanganates	$NaMnO_4$, $KMnO_4$
Peroxides	Na_2O_2, CaO_2, BaO_2, H_2O_2, organic peroxides and organic hydroperoxides

Perborates, percarbonates, perchromates, persulfates, etc.

Oxo-acids	$HClO_4$, H_2SO_4, HIO_4, $HMnO_4$, HNO_3, H_2O_2, etc.

The above salts become extremely hazardous in the presence of acids (H_2SO_4, HF, HNO_3, etc.) due to thermal decomposition of the liberated acid.

Oxidizing agents are not confined to oxygen-containing substances. A few examples are: F_2, BrF_3, Cl_2, Br_2, ICl_3, N_2F_4, NCl_3, (hydrocarbon) NCl_2, $SbCl_5$, $KICl_4$.

The mixing and reaction of these oxidizers with even slightly flammable materials must be done with great care and with proper provisions for maintaining temperature control. Remember that the hazards of weak oxidizing agents are increased by strong reducing agents. Hydrocarbon greases or oils must never be used in oxygen or halogen service.

(B) Explosives or Shock Sensitive Materials

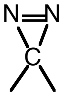
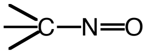
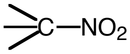
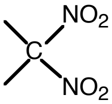
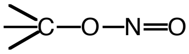
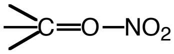
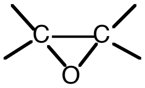
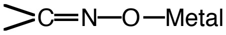
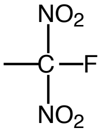
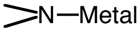
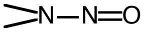
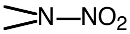
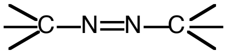
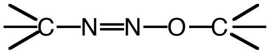
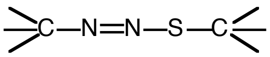
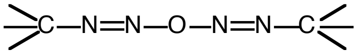
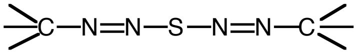
Certain atomic groupings are known by experience to be unstable or explosive. A Committee Review may be required for use of these materials. Waste containing any of the materials on the following pages requires consultation with the Safety Office for special disposal needs.

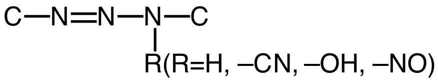
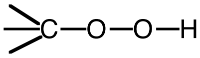
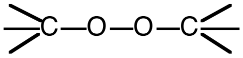
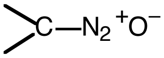
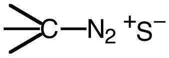
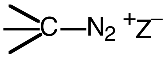
ATOMIC GROUPINGS THAT CHARACTERIZE EXPLOSIVE COMPOUNDS

Chemicals containing the following atomic groupings are known by experience to be unstable or explosive:

ATOMIC GROUPINGS THAT CHARACTERIZE EXPLOSIVE COMPOUNDS

Chemicals containing the following atomic groupings are known by experience to be unstable or explosive:

BOND GROUPINGS	CLASS
$-C\equiv C-$	Acetylenic Compounds
$-C\equiv C-\text{Metal}$	Metal Acetylides
$-C\equiv C-X$	Haloacetylene Derivatives
	Diazirines
	Diazo Compounds
	Nitroso Compounds
	Nitroalkanes, C–Nitro and Polynitroaryl Compounds
	Polynitroalkyl Compounds
	Acyl or Alkyl Nitrites
	Acyl or Alkyl Nitrates
	1, 2–Epoxides
	Metal Fulminates or aci-Nitro Salts
 $-C(NO_2)_2-F$	Fluorodinitromethyl Compounds
	N–Metal Derivatives
	N–Nitroso Derivatives
	N–Nitro Derivatives
	AZO Compounds
	Arenediazoates
	Arenediazo Aryl Sulphides
	Bis-Arenediazo Oxides
	Bis-Arenediazo Sulphides

BOND GROUPINGS	CLASS
 $C-N=N-N(R)-C$ R(R=H, –CN, –OH, –NO)	Trizaenes
$-N=N-N=N-$	High-Nitrogen Compounds Tetrazoles
	Alkylhydroperoxides, Peroxyacids
	Peroxides (Cyclic, Diacyl, Dialkyl), Peroxyesters
$-O-O-$Metal	Metal Peroxides, Peroxoacid Salts
$-O-O-$Non-metal	Peroxoacids
$N-Cr-O_2$	Amminechromium Peroxocomplexes
$-N_3$	Azides (Acyl, Halogen, Non-Metal, Organic
	Arenediazoniumolates
	Diazonium Sulphides and Derivatives, 'Xanthates'
$N^+-H\ Z^-$	Hydrazinium Salts, Oxosalts of Nitrogenous Bases
$-N^+-OH\ Z^-$	Hydroxylammonium Salts
	Diazonium Carboxylates or Salts
[N-Metal] $^+Z^-$	Aminemetal Oxosalts
Ar-Metal –X X-Ar–Metal	Halo-Arylmetals
$N-X$	Halogen Azides N-Halogen Compounds N-Haloimides
$-NF_2$	Difluoroamino Compounds N, N, N-Trifluoroalkylamidines
$-O-X$	Alkyl Perchlorates Chlorite Salts Halogen Oxides Hypohalites Perchloric Acid Perchloryl Compounds

XXI. Air- or Water-Sensitive Materials

Many Materials react with air or water to evolve heat, flammable or even explosive gases, such materials include:

Lithium: Li
Sodium: Na
Potassium: K
Calcium: Ca
Rubidium: Rb
Cesium: Cs

Alloys and amalgams of the above:

- Hydrides
- Nitrides
- Sulfides
- Carbides
- Borides
- Silicides
- Tellurides
- Selenides
- Arsenides
- Phosphides
- Acid Anhydrides
- Concentrated acids or alkalis

The metals react exothermally with water and evolve hydrogen, whereas nitrides through phosphides in the above list react to evolve volatile, flammable and/or explosive hydrides.

Many organic materials such as isocyanates, organometallics, acid chlorides, etc. react violently with water.

For commercial materials, consult the vendor-supplied Material Safety Data Sheet for information on incompatible materials.

A useful reference for laboratory techniques to safely handle these materials is *The Manipulation of Air-Sensitive Compounds*, 2nd edition, D.F. Shriver and M.A. Drezdson, Eds., John Wiley & Sons, Inc., New York, NY, 1986, pp. 384. Consult *Handbook of Reactive Chemical Hazards,* 3rd edition, by L. Bretherick, Butterworths, Boston, 1985, for further information concerning chemical hazards.

Metal-Halocarbon Hazards

Halogenated solvents (such as carbon tetrachloride, methylene chloride, perchlor, etc.) and fluorolubes (such as Kel-F grease) are generally considered to be "safe" materials (from the standpoint of flammability this is normally true). However, the reaction of some halogenated materials with certain metals may proceed with explosive violence.

In particular, aluminum, magnesium, sodium, potassium lithium, calcium, barium, titanium, and beryllium must be exposed to halocarbons with caution. If these materials are used as powders or in granular form the potential hazard is significantly increased.

The cleaning of aluminum or magnesium machine parts with chlorinated or fluorinated solvents must be reviewed beforehand to ensure that the proper solvent is used. Chlorinated solvent must be properly inhibited and used under appropriate conditions of temperature and moisture when in contact with any metal. Similarly, the lubrication of aluminum or magnesium parts with fluorolube and other halocarbon lubricants must be considered dangerous, and avoided.

Read the Material Safety Data Sheet supplied by the vendor for specific warnings of incompatible materials. Common materials may have very unexpected consequences in certain situations.

Appendix A: Hazardous Chemicals Data

The following listing of hazard properties of common commercial available gases is complied from National Fire Code 10th edition (1991), section 325 M - Fire Hazard Properties of Flammable Liquids, Gases, and Volatile Solids.

Many of these gases will be used in a chemical fume hood. See Appendix B for a listing of flammable materials with a flash point of 25˚C or less or auto-ignition temperatures of 250˚C or less. Contact the Safety Office with questions concerning any of these listings.

A sample of Common Chemicals is listed in the following table. The code is from the National Fire Prevention (NFP) Code. The first number relates to Health (blue) Hazards, the second number relates to Flammability (red), and the third is Reactivity (yellow). The number designation is taken from the manual of NFPA.

[Refer to Section XIII. Health Identification Diagram]

Note that **PLNR** means **Precautionary Labeling Not Required**.

Hazardous Chemicals Data

GAS	NFPA			Flam.	Inhal.	Eye/Skin Contact/ Absorption	Other and CNS effects
	H	F	R				
Acetylene	1	4	3	High	Low	PLNR	CNS Effects
Allene	1	4	0	High	Low	Low	
Ammonia, anhydrous	3	1	0	High	High	High	
Boron Trichloride	3	2	1	PLNR	High	High	
Butadiene (1,3-)	2	4	2	High	High	Low	Reg. carcinogen, blood effects

Butane	1	4	0	High	Moderate	PLNR	CNS effects, Irregular heartbeats
Butene-1 (3-Methyl)	1	4	0	High	Low	Low	
Butenes	1	4	0	High	Moderate	PLNR	CNS effects, irregular heartbeats
Carbon Monoxide	2	4	0	High	High	PLNR	Blood effects, teratogenic effects
Carbonyl Sulfide	3	4	1	High	High	High	
Chlorine	3	0	0	PLNR	High	High	oxidant
Chlorotrifluoroethylene		4	0	High	Moderate	Moderate	
Cyanogen	4	4	3	High	High	High	
Cyclopropane	1	4	0	High	Moderate	Low	
Deuterium	0	4	0	High	Low	PLNR	
Dimethyl Ether	2	4	1	High	Moderate	PLNR	CNS effects
Dimethylamine	3	4	0	High	High	Low	
Dimethylpropane (2,2)	0	4	0	High	Moderate	Low	
Ethane	1	4	0	High	Low	PLNR	
Ethyl Chloride	2	4	0	High	Moderate	Low	May cause irregular heartbeats
Ethylene	1	4	2	High	Low	PLNR	CNS effects
Ethylene Oxide	2	4	3	High	Moderate	Moderate	Regulated carcinogen, CNS, teratogenis effects
Hydrogen	0	4	0	High	Low	PLNR	
Hydrogen Bromide	3	0	0	PLNR	High	High	
Hydrogen Chloride	3	0	0	PLNR	High	High	
Hydrogen Fluoride	4	0	0	PLNR	High	High	
Hydrogen Iodide	3	0	0	PLNR	High	High	
Hydrogen Sulfide	3	4	0	High	High	PLNR	Blood effects
Isobutane	1	4	0	High	Moderate	PLNR	
Isobutylene	1	4	0	High	Moderate	PLNR	
Methane	1	4	0	High	Moderate	PLNR	
Methyl Bromide	3	0	0	PLNR	High	High	
Methyl Chloride	2	4	0	High	Moderate	PLNR	Reproductive effects
Methyl Mercaptan	2	4	0	High	Moderate	Moderate	
Monoethylamine	3	4	0	High	High	High	

Monomethylamine	3	4	0	High	Moderate	High	
Nitrogen	3	0	0	PLNR	Low	PLNR	
Nitrogen Trioxide	3	0	0	PLNR	High	High	Oxidant
Oxygen	3	0	0	PLNR	PLNR	PLNR	Oxidant
Phosgene	4	0	0	PLNR	High	High	
Phosphine	3	4	1	High	High	High	
Propane	1	4	0	High	Low	PLNR	Irregular heartbeats
Propylene	1	4	1	High	Low	PLNR	CNS effects
Sulfur Dioxide	2	0	0	PLNR	High	High	
Trimethylamine	2	4	0	High	Moderate	High	
Vinyl Chloride	2	4	1	High	High	Moderate	

Appendix B: Means of Lab Waste Disposal

UP THE HOOD: Nontoxic gases, unavoidable solvent vapors and toxic gases that get past traps. *No: concentrations of solvents by in-hood evaporation from open containers (this includes uncapped liquid waste containers), large amounts of HCl, H_2S, etc.*

DOWN THE DRAIN: Water, soap, nontoxic inorganic salts. *No: organics (including ethanol), toxic metals, odorous substances.*

TRASH CANS: Paper (if you can't recycle it), clean, empty, open containers, uncontaminated laboratory items (paper towels, Kimwipes, clean glass containers). *No: other stuff.*

BIG RED CANS: Organic solvents without significant dissolved solids. *No: air- or water-reactive compounds (such as acetic anhydride or TBSCl), phenol, pyridine, benzene.*

SEALED, PROPERLY LABELED, INDIVIDUAL CONTAINERS: Everything else, including aqueous solutions, aqueous-organic mixes, toxic metals, benzene, phenol, and pyridine. Separate hazard classes as much as possible. *No: anything that can be made less hazardous in lab, such as air- or water-reactive wastes, aqueous wastes at pH other than $pH \leq 2$ or $pH \geq 12$, regulated carcinogens, amalgams, or anything else acutely reactive or toxic. Neutralize until it becomes acceptable. Questions? Consult the group Safety Officer.*

LABELING: Several types of preprinted waste labels are available in each lab and from the group Safety Officer. The label for each container should give the name, room number, date of disposal, and telephone extension of someone who is familiar with the waste. Check all hazards that apply! Names, not formulas, of waste species should be given: “ethyl acetate” is acceptable, but “EtOAc” is not.

RED CAN LABELS: If any significant amount of solvent not already on the preprinted list is used, add its name to the list in the space provided. Extra labels are posted near each red can.

REMEMBER: Clearly and completely label anything that goes to the Safety Office, and be sure that all containers are sealed and that their exteriors are free from any waste.

Appendix C: Where to Put Specific Wastes

GASES AND VAPORS

- NON-TOXIC: up the hood
- TOXIC: HCl, H_2S, etc. Trap and neutralize whenever possible

SOLID WASTES

- NON-HAZARDOUS: Kimwipes, paper towels, gloves, etc. (not contaminated) go into the trash. Pipettes and test tubes go in glass boxes.

- GENERAL: Laboratory wastes contaminated with foreign residues that do not belong to a specific hazard category should be labeled with the contaminant's name (if practical should not be mixed together – disposal becomes difficult) in a container to go to the Safety Office.

- SPECIFIC HAZARDS: Toxic metals (such as Hg, Cd, Se, Te, Tl, Pb, Cr, Be, and Pu), "extremely hazardous" chemicals, and the like should be, in as small a volume as possible, placed in separate labeled containers to go to the Safety Office. If possible, turn it into something less hazardous in the lab.

- REGULATED CARCINOGENS: Destroy, place remainder in separate containers.

- SILICA GEL: Put in separate containers. Use the preprinted labels provided.

- EMPTY CHEMICAL CONTAINERS: Rinse with water – and let dry (dripping and wet containers upsets the custodian) possibly delabel – place in trash *with lids off!*

LIQUID WASTES – ORGANICS

- CLEAN: Solvents from rotovaps and from lightly loaded chromatography columns can go into the big red cans. No pyridine or benzene, and go easy on dimethyl sulfide, too.

- DIRTY: Solvents with a higher concentration of solutes go into labeled containers.

- SMELLY: Divalent sulfur or trivalent phosphorous compounds should be treated with bleach and placed into separate containers.

- REACTIVE OR HORRID: Air- or water-reactive and very nasty compounds should be quenched or given to the group Safety Officer for destruction.

- BASE BATHS: Neutralize with tech grade sulfuric acid. Decant supernatant into red cans, put sludge into a separate container.

LIQUID WASTES – AQUEOUS

- Neutralize any acids or bases to pH neutrality; down the drain unless insoluble materials are present – place in separate containers.

SPECIAL WASTES, OTHER CATEGORIES

- Neutralize or destroy to the greatest possible extent, dispose of separately. If unsure, consult with the group Safety Officer. The Safety Office knows the regulations concerning the transport (or illegality thereof) of wastes, but it is *our* responsibility to understand the chemistry of what we generate.

Appendix D: Destruction of Laboratory Wastes

THE NECESSITY

A few laboratory wastes may be disposed of by sending up the hood, flushing down the drain, or placing in the trash. Other wastes may be placed into properly labeled containers for disposal by the Safety Office. Some wastes, however, are so reactive, intensely toxic, or expensive to discard that they should be converted in the laboratory to more innocuous materials before they are sent to the Safety Office. In general, it is good practice whenever possible to transform any nasty substance into something less hazardous before disposal. Costs to the Institute will decrease, and future generations will thank you.

WHAT NEEDS TO BE DESTROYED

At a minimum, all compounds that are explosive; react with air or water violently, exothermically, or with gas evolution; regulated carcinogens; and other highly toxic compounds should be destroyed in the lab. In addition, substances that pose special hassles or excessive expense for the Safety Office can often be more conveniently or economically dealt with closer to the source, by the people who are most familiar with them.

AN IMPORTANT CONSIDERATION

Carry out all destruction procedures very cautiously! These wastes are often extremely reactive or toxic, and many of the destruction procedures involve powerful reagents and violent reactions. If following a procedure for the first time, always have someone in the room with you, and always wear the minimal safety gear of a lab coat, gloves and eye protection. For violent reactions, work behind a safety shield. If you are developing a destruction procedure on your own, work initially with small quantities, and scale up the reaction only gradually.

Remember that difficulties with vigorous and exothermic reactions become much more pressing as the scale increases.

WHERE TO FIND DESTRUCTION PROCEDURES

Destruction procedures for a fair sampling of commonly encountered wastes can be found in Lunn, G; Sanson, E.B. *Destruction of Hazardous Chemicals in the Laboratory,* John Wiley and Sons: New York, 1990. These procedures are well-documented, and tests for the completeness of destruction are also given. In addition, all chemicals in the Aldrich catalog have a code letter referring to a disposal procedure. In some cases, the procedure only instructs the reader to call the Technical Services Department at (800) 231-8377 (a toll-free number!) for specific information. The nice operator will be happy to read to you the complete disposal instructions. Procedures for handling and disposal of gases can be found in Beaker, W.; Mossman, A.L. *Matheson Gas Data Book, 5 ed.*; Matheson Gas Products: East Rutherford, NJ, 1971.

Several procedures for other types of wastes are as follows:

DESTRUCTION INSTRUCTIONS

AMALGAMS

These alloys of mercury with other, often active metals are useful because they provide a fresh surface containing the active metal, unsullied by passivating layers of oxidized crud. Laboratory destruction is necessary because contaminated mercury metal is almost universally not accepted by disposal firms.

In general, the procedure for destroying an amalgam is fully oxidize the active metal, and then to oxidize the remaining quicksilver with nitric acid. For most amalgams, this is fairly straightforward. Aluminum amalgam poses some special challenges for destruction, so its procedure is described in considerable detail.

ALUMINUM AMALGAM

Principle of Destruction

Aluminum metal is active enough to reduce water, but it is normally rendered passive by its inert oxide coating. In the amalgam, oxide formed does not adhere to the mercury surface, enabling reaction to continue. However, the alumina produced forms a solid mass which may entrap particles of mercury or aluminum amalgam.

It is first necessary to dissolve the existing precipitated alumina and to prevent any more from precipitating from the reaction of the aluminum amalgam. Hydrated alumina is hexacoordinate $[Al(OH)_3(H_2O)_3]$ and in strongly basic media becomes soluble aluminate $[Al(OH)_4(H_2O)_2]^{-}$. Thus, in basic solution, precipitate alumina will dissolve, and the aluminum in the amalgam will be oxidized directly to dissolve aluminate, leaving behind metallic mercury.

Occasionally an aluminum or aluminum amalgam sample will become passive to alkali. Fortunately, aluminum, like many other active metals, is attacked by strong mineral acid and precipitate hydrated alumina, with the same attendant problems of passivation and entrapment of metallic particles that are found in neutral solution. An exception is aluminum sulfate, which hydrolyzes only to a minor extent and which is fairly soluble in water. Consequently, sulfuric acid is often efficacious in oxidizing aluminum when caustic has failed.

Destruction Procedure

For amalgam and precipitated alumina initially formed from 100g of aluminum.

Place the aluminum amalgam and alumina into a 4l Erlenmeyer flask. Add 200 ml 50% aqueous sodium hydroxide (w/w). The aluminum particles will fizz. Heat to boiling on a hot plate. As the system is heated, any alumina powder should dissolve, and the hydrogen evaluation by the aluminum particles will become vigorous. Once the system is boiling, gradually add 450 ml plain water. This may result in extensive foaming, so keep a close watch. Adding more water will *not* make the foaming go down. Again, heat this mixture to boiling, and then allow to cool to room temperature. This takes several hours.

Once the mixture has cooled, it may consist of a large mass of white precipitated alumina, or a clear solution over liquid mercury, over steadily bubbling aluminum amalgam, or over an inactive mossy black solid. Follow the instructions for the appropriate condition.

- **A mass of precipitated alumina:** This is a result of not having enough base to turn all of the hydrated alumina formed into soluble aluminate. To dissolve the alumina, add plain water as needed to make a viscous slurry, and heat on a hot plate until boiling, add 50% NaOH until the precipitate dissolves. Allow to cool, and follow the instructions appropriate for the product obtained.

- **A clear solution over steadily bubbling aluminum amalgam:** Simply allow it to stand until the active aluminum has been consumed and the system falls under one of the other categories. If you are impatient, this process can be hastened by heating on a hot plate, adding water to keep an approximately, constant liquid level. Follow the instructions appropriate for the product obtained.

- **A clear solution over an inactive mossy black solid:** This inactive solid is probably passive aluminum covered with finely divided mercury metal or mercury (I) salts. Decant the supernatant and several rinsings with plain water into the waste bottle. Cover the solid with technical grade sulfuric acid. Vigorous gas evaluation should commence. If desired, add a few ml of nitric acid. When the reaction dies down, decant the supernatant into the waste bottle. Repeat this procedure until only liquid mercury remains, and then follow the instructions for liquid mercury.

- **A clear solution over liquid mercury:** Decant the supernatant and rinse several times with plain water into the waste bottle. Cover the mercury with nitric acid or a cocktail of about 10:5:1 (v/v/v) nitric acid; sulfuric acid; hydrochloric acid. The ensuing reaction should be vigorous and exothermic, with evolution of gaseous red-brown nitrogen oxides. Allow to stand for about a day. Decant the supernatant into the waste bottle; if any metallic mercury remains, repeat the procedure. Transfer *all* materials, including moderately insoluble salts, to the waste bottle.

Product Neutralization

Neutralize the strongly caustic mixture in the waste bottle by adding technical grade sulfuric acid, this reaction is violently exothermic, so wear protective gear (lab coat, glove, eye protection) and work behind a safety shield. A good rule of thumb is that the base will be about neutralized when so much alumina has precipitated that the formerly liquid solution becomes a gelled slurry. Test the pH and adjust, if needed, to between 6 and 8.

Allow this neutralized mass to cool, label the waste bottle, and take it to the stockroom for the Safety Office to dispose of it. On the label, check “Inorganics,” “Solids,” “Liquids,” “Aqueous Waste: pH” (report the pH), “Toxic,” “Mercury Salt,” and under “Identities of waste species,” write “water, precipitated alumina (mostly), sodium sulfate, sodium nitrate, sodium chloride, about 1 gram mercury salts (nitrate).”

Miscellaneous Notes

- **The Waste Bottle:** A four-liter glass jug such as used for solvents works well – acid jugs – 4 liters are coated to provide an extra level of protection. It can withstand the severely caustic solution before neutralization, and also the heat of the neutralization. Be careful, however, in transporting in chemical carrier; if it breaks, the contents will make a very inconvenient toxic mess.

- **Some Words on Decanting:** It is easy to pour an aqueous supernatant away from mercury when the supernatant volume is large. Once the bulk of the supernatant has been removed, however, it is easier to remove the remainder by pipette. With a little care, almost all of the aqueous phase can be removed without pipetting any of the very dense quicksilver.

- **How to Tell Mercury:** During swirling, pipetting, or decanting, there may be some dark solid carried along with the supernatant. Do not worry: you may dispose of this directly into the waste bottle, as it is not metallic mercury. Mercury, by virtue of its density, will pretty much stay on the bottom. It may appear as a shiny liquid metal or as a finely-divided black dust, but its reluctance to become swept up in water currents will give it away every time.

LITHIUM OR SODIUM AMALGAM

Treat as the unalloyed active metal. Under inert atmosphere, slowly add ethanol until no further reaction is seen, then cautiously add water to dissolve all non-mercury solids. Decant the supernatant away from the mercury (see “Some Words on Decanting” and “How to Tell Mercury”), then destroy the mercury with nitric acid. Combine all products bring to pH neutrality, and dispose in a properly labeled waste container.

ZINC AMALGAM

Zinc readily dissolves in dilute mineral acid. Place the amalgam in 1M HCl, and allow to stand until gas evolution has ceased. Decant the supernatant (see “Some Words on Decanting” and “How to Tell Mercury”), then destroy the mercury metal, and bottle, label, and dispose of the products as with lithium or sodium amalgam.

GRIGNARD AND ORGANOLITHIUM REAGENTS

For up to 1 mole-equivalent of reagent.

Equip a 5 liter 3-neck round bottom flask with a mechanical stirrer and flush with inert gas. Maintain under inert atmosphere (bubbler), surround the vessel with an ice bath (a metal bucket works well), and add the reagent. Dilute to a total volume of about 1.5 liters with technical grade high-boiling petroleum ether (ligroin). In one neck of the flask, set up a pressure-equalizer additional funnel containing about 500 ml 1:1 (v/v) ethyl acetate: ligroin. With moderate stirring, dropwise add the entire ethyl acetate solution. Some solid product will form. Continue to stir for about twenty minutes after the addition is finished.

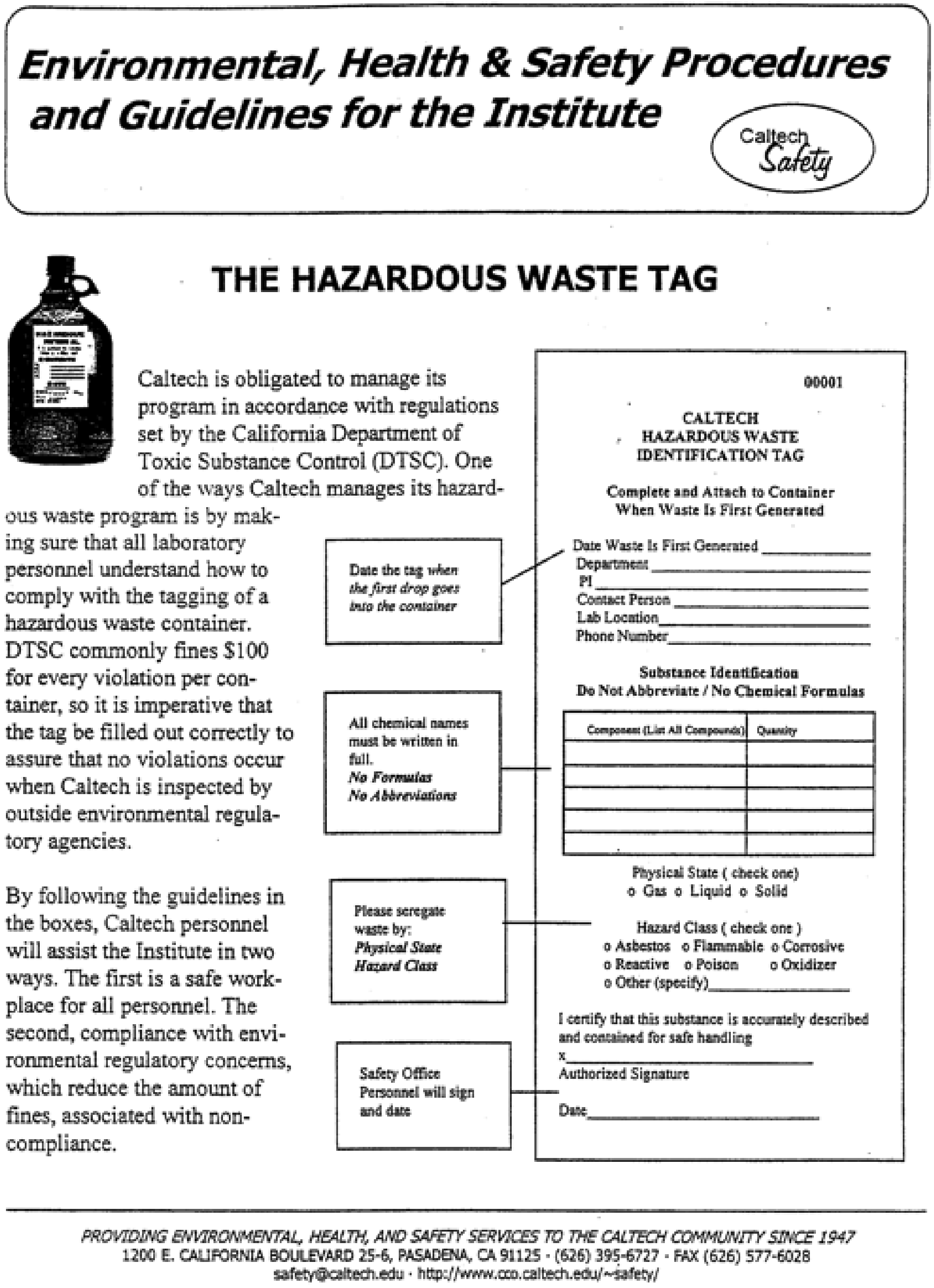
While still stirring the heterogeneous mixture, very cautiously (dropwise) add water, if a lithium reagent, or saturated ammonium chloride, if a Grignard reagent. Much more solid product will probably form. If it threatens to bind the mechanical stirrer, add more ligroin. When a separate aqueous phase can be seen at the bottom of the vessel (it may be necessary to remove the ice bath to see this), water can be added more freely. Carefully add your favorite mineral acid to fully dissolve the last of the solid (and especially important consideration if a Grignard reagant). Discard the organic phase as solvent waste, and titrate the aqueous phase to pH neutrality. An aqueous phase containing magnesium salts may be dumped down the drain, but lithium salts should probably be labeled for disposal by the Safety Officer.

TRIMETHYLSILYL CYANIDE

For 25 g.

In a fume hood and behind a safety shield, add the TMSCN dropwise to a 15% aqueous solution of sodium carbonate over ice. Wear adequate skin protection (gloves, lab coat) as spattering may occur. This procedure hydrolyzes the TMSCN to NaCn. Add household bleach, monitoring the pH (it should remain over 9). This will oxidize cyanide to cyanate. Allow this solution to stand overnight, then neutralize the pH (do not make it acidic or chlorine gas will effervesce), and dump down the drain.

Appendix E. Hazardous Waste Tag



Environmental, Health & Safety Procedures and Guidelines for the Institute

Caltech Safety

THE HAZARDOUS WASTE TAG

Caltech is obligated to manage its program in accordance with regulations set by the California Department of Toxic Substance Control (DTSC). One of the ways Caltech manages its hazardous waste program is by making sure that all laboratory personnel understand how to comply with the tagging of a hazardous waste container. DTSC commonly fines $100 for every violation per container, so it is imperative that the tag be filled out correctly to assure that no violations occur when Caltech is inspected by outside environmental regulatory agencies.

By following the guidelines in the boxes, Caltech personnel will assist the Institute in two ways. The first is a safe workplace for all personnel. The second, compliance with environmental regulatory concerns, which reduce the amount of fines, associated with non-compliance.

Date the tag *when the first drop goes into the container*

All chemical names must be written in full.
No Formulas
No Abbreviations

Please seregate waste by:
Physical State
Hazard Class

Safety Office Personnel will sign and date

00001

CALTECH
HAZARDOUS WASTE
IDENTIFICATION TAG

Complete and Attach to Container
When Waste Is First Generated

Date Waste Is First Generated ______________
Department ______________________________
PI _____________________________________
Contact Person ___________________________
Lab Location_____________________________
Phone Number____________________________

Substance Identification
Do Not Abbreviate / No Chemical Formulas

Component (List All Compounds)	Quantity

Physical State (check one)
○ Gas ○ Liquid ○ Solid

Hazard Class (check one)
○ Asbestos ○ Flammable ○ Corrosive
○ Reactive ○ Poison ○ Oxidizer
○ Other (specify)________________

I certify that this substance is accurately described and contained for safe handling
x______________________________
Authorized Signature

Date______________________________

PROVIDING ENVIRONMENTAL, HEALTH, AND SAFETY SERVICES TO THE CALTECH COMMUNITY SINCE 1947
1200 E. CALIFORNIA BOULEVARD 25-6, PASADENA, CA 91125 · (626) 395-6727 · FAX (626) 577-6028
safety@caltech.edu · http://www.cco.caltech.edu/~safety/

Appendix F: Fume Hood Guidelines

The protection afforded by a fume hood is only as good as the work practices of the hood user. The following are general guidelines to be followed when working in the hood.

1. Know the toxic properties of the chemicals with which you work. Be able to identify signs and symptoms of overexposure.
2. Mark a line with tape six inches behind the sash and keep all chemicals and equipment behind that line during experiments. This will keep vapors from escaping the hood when air currents from people walking past the hood interfere with air flow at the face of the hood.
3. Keep the sash completely lowered anytime there is no “hands-on” part of the experiment in progress or whenever the hood is on and unattended.
4. Never use a hood unless there is some indication that it is operating. A tissue or Kimwipe taped to the sash or inside the hood provides a reasonable indication of airflow.
5. The hood is not a substitute for personal protective equipment. Wear a lab coat, gloves, and safety glasses as appropriate.
6. Visually inspect the baffles (openings at the top and rear of the hood) to be sure the slots are open and unobstructed.
7. Do not block baffles. If large equipment is in the hood, put it on blocks to raise it approximately two inches so that air may pass beneath it.
8. Do not use an active hood as a storage cabinet. Keep only the materials necessary for the experiment inside the hood. If chemicals need to be

stored in the hood for a period of time, install shelves on the side of the hood, away from the baffles.

9. Keep the sash clean and clear.
10. Clean all chemical residue in the hood after each use.
11. All electrical devices should be connected outside the hood to avoid sparks that may ignite a flammable or explosive chemical.
12. DO NOT USE A FUME HOOD AS A WASTE DISPOSAL DEVICE. Use traps and condensers whenever possible to collect vapors and fumes. Never use a hood to evaporate solvents. Instead, collect the solvent and dispose of it as hazardous waste.
13. DO NOT USE A FUME HOOD FOR ANY FUNCTION FOR WHICH IT IS NOT INTENDED. Certain chemicals or reactions require specially constructed hoods. Examples are perchloric acid or high-pressure reactions. If there are any questions about the capabilities of a particular hood, contact the Safety Office, extension 6727.

Appendix G: Working with Cryogenics

Cryogenic fluids are characterized by having a boiling point of less than -73 degrees C (-100 degree F). The boiling points of carbon dioxide and nitrogen are -78.5 degrees C and -195.8 degrees C, respectively. Another physical property of cryogenic fluids is the high-volume-expansion ratio in the liquid-to-gas phase. This ratio is 553 to 1 for carbon dioxide and 696 to 1 for nitrogen.

Using cryogenic fluids improperly may produce physical and personal hazards that are not always obvious. The primary hazard to people is skin or eye contact with splashing liquid as it warms and expands. Injuries similar to a burn will result. Safety goggles or a face shield should be worn. Clean, insulated gloves that can be easily removed are recommended. Arm and leg protection is also recommended.

All cryogenic fluids are capable of causing asphyxiation without warning by displacing oxygen-containing air. Areas where they are used or stored should be adequately ventilated. These fluids should not be used in closed rooms or other enclosed spaces.

Also, cryogenic fluids are capable of condensing oxygen from the air, causing oxygen enrichment or oxygen entrapment in confined spaces, which may result in increased flammability and subsequent explosion hazard.

Liquified gases are generally stored at atmospheric pressure in an insulated container, which keeps them near their boiling point, with some gas present. The large expansion in volume that takes place when the liquid becomes a gas means that pressure can build up in an unvented or unrelieved container and in transfer lines and piping. System design and maintenance must take this expansion ratio into account. Only containers designed for cryogenic fluids should be used.

The selection of materials to be used with cryogenics is important because of the changes in physical properties of materials at very low temperatures. Some materials become extremely brittle. Chemical interactions between the cryogenic liquid and its container or equipment must also be evaluated.

The Dewar flask is the most common container used for storage and transfer of cryogenic fluids. When using the Dewar, follow these procedures.

- Cover the Dewar with a cap that allows escape of built-up pressure and keeps air and moisture out.
- Transfer cryogenic liquids from large Dewar vessels with special transfer tubes designed for the particular application.
- Tipping or tilting to pour the liquid may damage large Dewars.
- Do not use heat guns or similar equipment to warm transfer tubing quickly for disconnection.
- Handle containers carefully to protect the vacuum insulation system of Dewars.
- Place large Dewars on dollies that move freely so there is no possibility of personal injury or damage to the supported Dewars.

Due to extremely cold temperatures of cryogenic liquids and “boil-off” gases, use the following personal protective equipment (PPE):

- When cryogenics are present, safety glasses with side shields

- When cryogenics are poured or transferred:
  - Safety glasses and a full face shield
  - Loose-fitting thermal gloves
  - Long sleeved clothing (lab coat)
  - Long pants
  - Closed-toe shoes

Anyone using cryogenic material must receive instruction in using cryogenic materials safely from their lab supervisor or safety officer.

If there is a cryogenic spill, immediately leave the area. If you believe the cryogen has caused significant oxygen depletion, do not re-enter the area unless the oxygen content of the atmosphere is at least 19.5% and there is no flammable or toxic mixture present.

Appendix H: Vacuum Transfers and Condensation of Liquid Oxygen

The explosion that may result from liquid oxygen condensation during a prototypical vacuum transfer is very forceful, leading to the possibility of a serious injury. The CCE Division Safety Committee makes the following recommendations when dealing with the condensation of liquid oxygen:

1. Guidelines for carrying out a vacuum transfer experiment
2. Procedure for dealing with a situation in which liquid oxygen has or may have been condensed accidentally.

RECOMMENDATIONS

Use extreme caution when using liquid nitrogen as a coolant for a cold trap. If the system under vacuum is open to the atmosphere while the cooling bath is still in contact with the trap, **oxygen may condense in the receiving flask**. Liquid oxygen can then either react in the presence of organic material or build up pressure as it vaporizes to cause an explosion.

If you suspect the presence of liquid oxygen, ***you are in immediate danger***, as are those within the vicinity of the working area. Make sure that the hood sash is down, or that a blast shield is in front of the flask. Isolate the area by notifying all lab occupants, and immediately notify your supervisor and the Safety Office at extension 6727.

Consider dry ice cooling as an alternate method to liquid nitrogen. Add dry ice slowly to the liquid portion of the bath to avoid foaming.

Monitor the line pressure before starting and during a vacuum transfer. See accompanying vacuum transfer guidelines. If the pressure is too high, assume you have a liquid oxygen problem.

Cold traps should be checked frequently and not left unattended.

Always lower the fume hood sash and position the blast shields for maximum effect. Keep the fume hood as clear as possible by doing regular housekeeping maintenance.

Use appropriate gloves and a face shield to avoid skin contact with cryogenic liquids, equipment, and baths.

Vacuum Transfers

Vacuum transfers or distillations are a common and necessary aspect of many experimental chemistry labs. Liquid nitrogen is often used to cool the receiver flask due to its ready availability in labs, its effectiveness, and the speed with which the transfer occurs.

At atmospheric pressure many gases, including oxygen, condense at the temperature of liquid nitrogen, ca. –196 °C, thus presenting a serious hazard. The boiling point of liquid oxygen at 1 atmosphere of pressure is **–183 °C**.

Whenever possible choose a dry ice bath (with isopropanol ethanol or acetone as the bath solvent) to cool the receiving flask during vacuum transfers.

If liquid nitrogen must be used, as is the case for very volatile solvents, for certain NMR experiments, etc., take the following precautions to avoid liquid oxygen condensation:

1. Prior to cooling your receiver flask, ensure that the system holds its vacuum with some suitable pressure reading device, such as a monometer or a vacuum gauge. It should hold its pressure for a reasonable length of time (ca. 30 minutes) in order to be trustworthy. If it does not, locate the problem and fix it before attempting a vacuum transfer, seeking help or advice from your adviser if necessary.

2. Monitor the pressure of the static system during the transfer and note if it rises higher than you expect, or if the transfer of liquid slows dramatically or stops entirely. If it does, there may be a leak, which would prevent the solvent from transferring and would allow oxygen to condense within the receiver flask being stored in liquefied nitrogen. Never leave a vacuum transfer experiment for extensive periods unattended — and ***always keep the hood sash down*** during the process.

Dealing with liquefied oxygen.

At the point you realize liquid oxygen may have condensed ***you are in immediate danger***, as are those within the vicinity of the working area. Make sure that the hood sash is down, or that a blast shield is in front of the flask if the operation is not being executed within a hood.

1. Inspect the system, do so taking as many precautions as possible. Admittedly, this is a difficult situation and preventing liquid oxygen condensation is the only true solution. However, experienced researchers in several laboratories, both here at Caltech and in other departments, have adopted strategies that have proven dependable in the past.

2. Try to ensure that the liquid nitrogen dewar in which the receiver flask/vessel resides has an ample amount of liquid nitrogen in order to maintain a temperature of ca. **–196 °C**. This is essential to ensure that the liquefied oxygen remains cold and condensed. Warming of the liquid oxygen could result in a pressure buildup and/or a violent oxidation reaction, if organic material is also present in the flask.

3. At this stage, several options are available:
    a. Further venting the system to the open atmosphere, such as by opening a stopcock, is not advised as this provides an ample

supply of oxygen to the system and may serve to exacerbate the problem. The downfall of this strategy is that an explosion may well result if there are organic reagents within the flask

b. After ensuring that the dewar is filled with liquid nitrogen and that the flask remains submerged, try to locate the leak. If it can be fixed (as when a joint has slipped apart or a stopcock is accidentally opened), quickly seal the leak and open the system to dynamic vacuum. Sometimes the leak is present due to broken glassware, such as a snapped stopcock. You need to establish if the leak can be sealed effectively. If not, clear the area immediately.

4. If you have fixed or attempted to fix a leak, your manometer or vacuum gauge will tell you if the pressure lowers appropriately. If this is the case, pump on the isolated system under dynamic vacuum in order to gradually boil away the liquid oxygen. According to the CRC, liquid oxygen has a vapor pressure of 100mm at **-199 °C**, meaning that even with a relatively poor dynamic vacuum it may be pumped away effectively at the temperature of liquid nitrogen.

5. Once the system is under vacuum clear the area. The entire system should be regarded as an explosive danger until **no liquid oxygen remains** (e.g., the pressure reaches the maximum attainable vacuum for your system, as indicated by a manometer).

6. After the liquid oxygen has been completely removed, solicit the assistance of your supervisor or another qualified researcher. Remove the liquid nitrogen dewar, then detach the flask from the vacuum line and allow it to warm slowly behind a blast shield.

Appendix I: Segregation of Incompatible Substances

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

Examples of Incompatible Chemicals

Chemical	**Incompatible with**
Acetic Acid	Chromic acid, nitric acid, perchloric acid, peroxides, permanganates
Acetylene	Chlorine, bromine, copper, fluorine, silver, mercury
Acetone	Concentrated nitric acid and sulfuric acid mixtures
Alkali and alkaline earth metals	Water, carbon tetrachloride or other chlorinated hydrocarbons, i.e., powdered aluminum or magnesium, carbon dioxide, halogens, calcium, lithium, sodium, potassium.
Ammonia (anhydrous)	Mercury, chlorine, calcium hypochlorite, iodine, bromine, anhydrous HF
Ammonium nitrate	Acids, powdered metals, flammable liquids, chlorates, nitrites, sulfur, finely divided organics or combustibles
Aniline	Nitric acid, hydrogen peroxide
Arsenical materials	Any reducing agent
Bromine	See Chlorine

Calcium Oxide	Water
Carbon (activated)	Calcium hyperchlorite, 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
Flammable liquids	Ammonium nitrate, chromic acid, hydrogen peroxide, nitric acid, sodium peroxide, halogens
Fluorine	Everything
Hydrocarbons (such as butane, propane)	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
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, brass, any heavy metals
Nitrates	Acids
Nitroparaffins	Inorganic bases, amines
Oxalic acid	Silver, mercury
Oxygen	Oils, grease, hydrogen, flammable liquids, solids, or gases
Perchloric acid	Acetic anhydride, bismuth and its alloys, alcohol, paper, wood, grease, oils
Peroxides, organic	Acids (organic or mineral). Avoid friction, store cold.
Phosphorous (white)	Air, oxygen, alkalis, reducing agents
Potassium	Carbon tetrachloride, carbon dioxide, water
Potassium chlorate	Sulfuric and other acids
Potassium perchlorate (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 compunds of light metals, such as sodium, lithium)
Tellurides	Reducing agents

Appendix J: Chemical Resistance Chart

Explanation of Ratings Chemical Protective Clothing Performance Index Rating (CPC)

Breakthrough detection times (BDT) are given in minutes. CPC index ranges are based on the Forsberg system which relies on both break through time and permeation rates to establish a rating system for chemical protective clothing. The ratings range from 0 to 5, with 0 being the best and 5 being the worst.

0	Best and safest selection of unlimited exposure.
1	Next best selection for unlimited exposure.
2	Sometimes satisfactory. Good for limited exposure.
3	Poor Choice. Not for heavy exposure.
4	Very poor. For splashes only.
5	Not recommended.

Chemical by Class	Neoprene		Nitrile		Rubber		PVC		Butyl		Viton	
	BDT	CPC	BDT	CPC	BDT	CPC	BDT	CPC	BDT	CPC	BDT	CPC
Aliphatic Solvents												
1. Cyclohexane	21	2	9	0	55	5	13	3	ND	4	NR	0
2. Gasoline(Unleaded)		46	3	46	0	NR	5	22	3	NR	5	ND
	0											
3. Heptane	ND	0	ND	0	24	3	39	4	23	4	ND	0
4. Hexane	173	2	234	0	21	4	29	3	13	5	ND	0
5. Isooctane	ND	0	ND	0	57	3	114	3	56	4	ND	0
6. Kerosene	ND	0	ND	0	NR	5	ND	0	94	4	ND	0
7. Petroleum Ethers	99	2	ND	0	5	5	19	4	15	4	ND	0
Acids, Organic												
8. Acetic 84%	ND	0	240	5	ND	0	300	2	ND	0	ND	0
9. Formic 90%	ND	0	75	0	ND	0	ND	0	ND	0	120	0
Acids, Mineral												
10. Battery 47%	ND	0	ND	0	ND	0	ND	0	ND	0	ND	0
11. Hydrochloric 37%	ND	0	ND	0	ND	0	ND	0	ND	0	ND	0
12. Hydrofluoric 48%	ND	0	60	3	45	3	110	2	ND	0	185	1
13. Muriatic 10%	ND	0	ND	0	ND	0	ND	4	ND	0	ND	0
14. Nitric 70%	ND	0	NR	5	ND	0	240	5	ND	0	ND	0
15. Sulfuric 97%	ND	0	180	3	ND	0	210	5	ND	0	ND	0

Chemical by Class	Neoprene		Nitrile		Rubber		PVC		Butyl		Viton	
	BDT	CPC	BDT	CPC	BDT	CPC	BDT	CPC	BDT	CPC	BDT	CPC
Alcohols												
16. Amyl	ND	0	ND	0	ND	0	116	2	ND	0	ND	0
17. Butyl	ND	0	ND	0	ND	0	155	2	ND	0	ND	0
18. Cresols	ND	0	NR	5	371	2	ND	0	ND	0	ND	0
19. Ethyl	ND	0	225	4	ND	0	66	2	ND	0	ND	0
20. Methyl	226	1	28	3	82	2	39	4	ND	0	ND	0
21. Isobutyl	ND	0	ND	0	ND	0	ND	2	ND	0	ND	0
Aldehydes												
22. Acetaldehyde	21	3	NR	5	55	3	13	5	ND	0	NR	5
23. Benzaldehyde	93	3	NR	5	81	3	NR	5	ND	0	ND	0
24. Formaldehyde	ND	0	ND	0	ND	0	ND	0	ND	0	ND	0
25. Furfural	165	2	NR	5	ND	0	85	3	ND	0	298	3
Alkalis												
26. Ammonium Hydroxide	ND	0	240	3	120	3	60	4	ND	0	ND	0
27. Potassium Hydroxide	ND	0	ND	0	ND	0	ND	0	ND	0	ND	0
28. Sodium Hydroxide	ND	0	ND	0	ND	0	ND	0	ND	0	ND	0
Amides												
29. Dimethylacetamide	84	3	NR	5	29	4	51	4	ND	0	NR	5
30. Dimethylformamide	100	3	NR	5	ND	0	NR	5	ND	0	NR	5
31.N-MethylPyrrolidone	ND	0	34	3	ND	0	140	4	ND	0	NR	5
Amines												
32. Aniline	32	3	NR	5	1	4	71	3	ND	0	ND	0
33. Butylamine	NR	5	NR	5	45	3	15	3	45	3	NR	5
34. Diethylamine	23	5	60	5	60	5	107	4	30	3	9	5
Aromatic Solvents												
35. Benzene	15	5	16	4	NR	5	13	5	34	4	ND	0
36. Toluene	25	4	26	4	NR	5	19	4	22	4	ND	0
37. Xylene	37	4	41	4	NR	5	23	3	NR	5	ND	0
Chlorinated Solv.												
38. Carbon Tetrachloride	73	4	ND	0	NR	5	46	4	53	4	ND	0
39. Chloroform	23	4	6	5	NR	5	10	5	21	4	ND	0
40. Methylene Chloride	NR	5	4	5	NR	5	NR	5	20	4	113	3
41. Perchloroethylene	40	4	ND	0	NR	5	NR	5	28	4	ND	0

Chemical by Class	Neoprene		Nitrile		Rubber		PVC		Butyl		Viton	
	BDT	CPC	BDT	CPC	BDT	CPC	BDT	CPC	BDT	CPC	BDT	CPC
42. Trichloroethylene	12	5	9	5	NR	5	NR	5	13	5	ND	0
43. 1,1,1-Trichloroethane	51	4	49	4	NR	5	52	3	72	4	ND	0
Esters												
44. Amyl Acetate	110	3	77	4	NR	5	NR	5	158	3	NR	5
45. Ethyl Acetate	24	4	30	4	72	4	5	5	212	2	NR	5
46. Methyl Methacrylate	27	3	NR	5	77	3	NR	5	63	3	NR	5
Ethers												
47. Cellosolve Acetate		228	3	47	4	107	3	64	4	ND	0	NR
	5											
48. Ethyl Ether	12	5	33	4	11	5	14	5	19	5	29	5
49. Tetrahydrofuran	13	5	5	5	NR	5	NR	5	24	4	NR	5
Gases												
50. Ammonia, Anhydrous	29	2	336	1	4	4	19	3	ND	0	ND	0
51. 1,3-Butadiene	33	3	ND	0	25	3	24	3	473	2	ND	0
52. Chlorine	ND	0	ND	0	ND	0	360	2	ND	0	ND	0
53. Ethylene Oxide	21	4	17	5	1	5	1	5	189	2	48	4
54. Hydrogen Fluoride		210	2	1	5	142	1	1	5	ND	0	6
	3											
55. Methyl Chloride	84	1	ND	0	52	2	ND	0	ND	0	ND	0
56. Vinyl Chloride	7	4	ND	0	2	4	19	3	268	1	ND	0
Ketones												
57. Acetone	35	3	3	5	9	5	7	5	ND	0	NR	5
58. Methyl Ethyl Ketone	30	3	NR	5	12	5	NR	5	202	2	NR	5
59. MIBK	41	3	5	5	38	4	NR	5	292	2	NR	5
Nitriles												
60. Acetonitrile	65	3	6	5	16	3	24	4	ND	0	NR	5
61. Acrylonitrile	27	3	NR	5	48	3	14	5	ND	0	55	4

Appendix K: Safety Committee Recommendations Regarding the use of Solvent Stills

Solvent stills have long been a source of laboratory accidents. Still related explosions and fires have caused many of the most serious accidents across the country over the past few decades. A number of these accidents have been deadly. We are committed to reducing the number of accidents at Caltech, and as such the CCE Division Safety Committee recommends the following protocol for the use of heated solvent stills.

1. *Avoid using a solvent still if at all possible.* Many chemical suppliers now sell dry solvents, which are packed under inert atmospheres (e.g., *DrySolv*, *SureSeal*, etc.). These may be suitable for many laboratory applications. Alternatively, you may take advantage of the available shared solvent list for use of small amounts of solvent on a temporary basis. Finally, for larger more constant use, the Committee strongly advises the construction of a suitable solvent purification system in your laboratory. Consult with your PI about the appropriate course of action.

2. If a solvent still is the only course of action, consult a suitable guidebook for a safe method of purification. For example:
    a. Purification of Laboratory Chemicals by W. L. F. Armarego, D. D. Perrin.
    b. The Chemist's Companion: A Handbook of Practical Data, Techniques, and References by Arnold J. Gordon, Richard A. Ford

3. These are excellent reference texts and describe a number of purification procedures for many common solvents and reagents.

4. When searching for a suitable drying agent, choose the least reactive reagents that are suitable for the job. For example, choose molecular sieves *over* calcium hydride *over* sodium metal. This will make the solvent still safer and the cleanup easier.
5. The use of the following drying agents in solvent stills is *strictly prohibited*:

  a. Lithium Aluminum Hydride ($LiAlH4$)
  b. Potassium metal (K)

6. Procedures that call for the use of these materials for the drying of solvents are outdated, and should be abandoned. See item #2.

7. 5. Clean-up of solvent stills should be carried out in an appropriate fashion depending on the drying agent and solvent employed. Remember that all stills should be viewed with extreme caution and treated with care as with any chemical reactions.

Appendix L: Compressed Gas Association Connection Chart for Regulators

CYLINDER GAS TYPE	CHEMICAL SYMBOL	CGA CONNECTION Standard/Alternate
Acetylene	C_2H_2	510/300
Air	----	590/346
Allene	CH_2:C:CH_2	510
Ammonia Anhydrous	NH_3	240/705
Ammonia (VHP)	---	660
Antimony Penta Fluoride	SbF_5	330
Argon	Ar	580
Argon (Research Grade)	---	590
Arsine	AsH_3	350/660
Boron Trichloride	BCl_3	660/330
Boro Trifluoride	BF_3	330
Bromine Pentafluoride	BrF_5	670
Bromine Trifluoride	BrF_3	670
Bromoacetone	$BrCH_2COCH_3$	300/660
Bromochlorodifluoromethane	$CBrClF_2$	668/660
Bromochloromethane	CH_2BrCL	668/660
Bromotrifluoroethylene	Br FC:CF_2	510/660
Bromotrifluoromethane	$CBrF_3$	668/320, 660
1,3 - Butadiene	CH_2:CHCH:CH_2	510
Butane	$CH_3CH_2CH_2CH_3$	510
Butenes	CH_3CH_2CH:CH_2	510
Carbon Dioxide	CO_2	320
Carbon Monoxide	CO	350
Carbonyl Fluoride	COF_2	660/750
Carbonyl Sulfide	COS	330
Chlorine	CL_2	660
Chlorine Pentafluoride	CLF_5	670
Chlorine Trifluoride	ClF_3	670
Chlorodifluoroethane	$CH_3CCL\ F_2$	510/660
Chlorodifluoromethane	$CH\ Cl\ F_2$	660/668

CYLINDER GAS TYPE	CHEMICAL SYMBOL	CGA CONNECTION Standard/Alternate
Chlorofluoromethane	CH_2 Cl F	510
Chloroheptafluorocyclobutane	C_4F_7Cl	660/668
Chloropentafluoroethane	C_2CLF_5	668/660
Chlorotrifluoromethane	$CClF_3$	668/320,660
Cyanogen	C_2N_2	750/660
Cyanogon Chloride	CNCl	750/660
Cyclobutane	C_4H_8	510
Cyclopropane	C_3H_6	510
Deuterium	D_2	350
Deuterium Chloride	DCl	330
Deuterium Fluoride	DF	330
Deuterium Selenide	D_2 Se	350 / 330
Deuterium SulFide	D_2S	330
Diborane	B_2H_6	350
Dibromodifluoroethane	$C_2H_2Br_2F_2$	668/660
Dibromodifluoromethane	CBr_2F_2	668/660
1,1 - Difluoroethylene	FCH:CHF	320
Dichlorosilane	H_2 Si Cl_2	330/510
Diethylzinc	$(C_2H_5)_2Zn$	750
Dimethylamine	$(CH_3)_2NH$	705/240
Dimethyl Ether	CH_3OCH_3	510
2,2 Dimethyl Propane	$C(CH_3)_4$	510
Diphosgene	$ClCO_2CCl_3$	750/660
Ethane	C_2H_6	350
Ethane (Research Grade)	---	350
Ethylacetylene	CH_3CH_2:CH	510
Ethylchloride	CH_3CH_2Cl	510/300
Ethyldichloroarsine	$C_2H_5AsCl_2$	750/660
Ethylene	CH_2:CH_2	350
Ethylene Oxide	C_2H_4O	510
Ethyl Ether	$(C_2H_5)_2O$	510

CYLINDER GAS TYPE	CHEMICAL SYMBOL	CGA CONNECTION Standard/Alternate
Ethyl Fluoride	C_2H_5F	750/660
Fluorine	F_2	679/670
“Freon 12 “ (Dicholordifluoromethane)	Cl_2	660
“Freon 13 “ (Chlorotrifluoromethane)	$CClF_3$	320
“Freon 1381” (Bromotrifluoromethane)	$CBrF_3$	320
“Freon 14 “ (Tetrafluoromethane)	CF_4	320
“Freon 22” (Chlorodifluoromethane)	$CHClF_2$	660/620
“Freon 114” (1,2 – Dichlorotetrafluoroethane)	$Cl\ F_2\ CCCl\ F_2$	660
“Freon 116 “ (Hexafluoroethane)	C_2F_6	320
“Freon 8318” (Octafluorocyclobutane)	C_4F_8	660
“Genetron 21” (Dichlorofluoromethane)	$CHCl_2F$	660
“Genetron 23” (Fluoroform)	$CH\ F_3$	320
“Genetron115” (Monochloropentafluoroethane)	$Br\ F_2\ CCF_3$	660
“Genetron 152A “ (1,1 – Difluoroethane)	$F\ CH_2\ CH_2\ F$	660
Germane	$Ge\ H_4$	660/750
Helium	He	580/677
Heptafluorobutyronitrile	C_4F_7N	750/660
Hexafluoracetone	C_3F_6O	660/330
Hexafluorocyclobutene	C_4F_6	750/660
Hexafluorodimethyl Peroxide	CF_3OOCF_3	755/660
Hexafluoroethane	C_2F_6	660/668
Hexafluoropropylene	$CF_3CF{:}CF_2$	668/660
Hydrogen	H_2	350
Hydrogen Bromide	HBr	330
Hydrogen Chloride	HCL	330
Hydrogen Cyanide	HCN	750/160
Hydrogen Fluoride	HF	330/660
Hydrogen Iodide	HI	330/660
Hydrogen Selenide	H_2Se	350/660
Hydrogen Sulfide	H_2S	330

CYLINDER GAS TYPE	CHEMICAL SYMBOL	CGA CONNECTION Standard/Alternate
Iodine Pentafluoride	IF_5	670
Isobutane	C_4H_{10}	510
Isobutylene	C_4H_8	510
Krypton (research Grade)	Kr	590
"Manufactured Gas B"	---	350
"Manufactured Gas C"	---	350
Lewsite	$ClCH:CHAsCL_2$	750/660
Methane	CH_4	350
Methylacetylene	$CH_3C:CH$	510
Methyl Bromide	CH BR	320/660
3-Methyl – 1 -butene	$(CH_3)_2CHCH:CH_2$	510
Methyl Chloride	CH_3Cl	660/510
Methyldichloroarsine	CH_3AsCl_2	750
Methylene Fluoride	CH_2F_2	320
Methyl Ethyl Ether	$CH_3OC_2H_5$	510
Methyl Fluoride	CH_3F	350
Methyl Formate	$HCOOCH_3$	510/660
Methyl Mercaptan	CH_3SH	330/750
Monoethylamine	$CH_3CH_2NH_2$	240/705
Monomethylamine	CH_3NH_2	240/705
Mustard Gas	$S(C_2H_4Cl)_2$	750/350
Natural Gas	---	350/677
Neon	Ne	590/580
Nickel Carbonyl	$Ni\ (CO)_4$	320/750
Nitric Oxide	NO	660/755, 160
Nitrogen	N_2	580
Nitrogen (Research Grade)	---	590
Nitrogen Dioxide	NO_2	660/160
Nitorgen Trifluoride	NF_3	679
Nitrogen Trioxide	N_2O_3	660/160
Nitrosyl Chloride	NOCl	660/330

CYLINDER GAS TYPE	CHEMICAL SYMBOL	CGA CONNECTION Standard/Alternate
Nitrosyl Fluoride	NOF	330
Nitrous Oxide	N_2O	326
Nitryl Fluoride	NO_2F	330
Octafluorocyclobutane	C_4F_8	660/668
Octafluoropropane	C_3F_8	660/668
Oxygen	O_2	540
Oxygen Difluoride	OF_2	679
Ozone	O_3	660/755
Pentaborane	B_5H_9	660/750
Pentachlorofluoroethane	CCl_3CCl_2F	668/660
Pentafluoroethyl Iodine	CF_3CF_2I	668/660
Pentafluoropropionitrile	CF_3CF_2CN	750/660
Perchloryl Fluoride	ClO_3F	670
Perfluorobutane	C_4F_{10}	668
Perfluorobutene – 2	C_4F_8	660
Phenylcarbylamine Chloride	$C_6H_5N : CCl_2$	330/660
Phosgene	$COCl_2$	660
Phosphine	PH_3	660/350
Perfluoropropane	---	660
Phosphorous Pentafluoride	PF_5	330
Phosphorous Trifluoride	PF_3	330
Propane	C_3H_8	510
Propylene	C_3H_6	510
Silane	SiH_4	350/510
Silicon Tetrafluoride	SiF_4	330
Stibine	SbH_3	350
Sulfur Dioxide	SO_2	660/668
Sulfur Hexafluoride	SF_6	590/668
Sulfur Tetrafluoride	SF_4	330
Sulfuryl Fluoride	SO_2F_2	660/330
1, 1, 1, 2 – Tetrachlorodifluoroethane	$C_2FI_4F_2$	668/660

CYLINDER GAS TYPE	CHEMICAL SYMBOL	CGA CONNECTION Standard/Alternate
1, 2, 2, 2, - Tetrafluorochloroethane – 1	C_2HClF_4	668/660
Tetrafluoroethylene	C_2F_4	350/660
Tetrafluorohydrazine	N_2F_4	679
Tetrafluoromethane	CF_4	580/320
Tetramethyllead	$(CH_3)_4Pb$	750/350
Trichlorofluoromethane	CCl_3F	668/660
Trichlorotrifluoroethane	CF_3CCl_3	668/660
Triethylaluminum	$(C_2H_5)_3Al$	750/350
Triethylborane	$(CH_5)_3B$	750/350
Trifluoroacetonitrile	CF_3CN	750/350
Trifluoroacetyl Chloride	CF_3COCl	330
1, 1, 1 – Trifluoroethane	CH_3CF_3	510
Trifluoroethylene	C_2F_3H	510
Trifluoromethyl Hypofluorite	CF_3OF	679
Trifluoromethyl Iodide	CF_3I	668/660
Trimethylamine	$(CH_3)_3N$	240/705
Trimethylstibine	$(CH_3)_3Sb$	750/350
Tungsten Hexafluoride	WF_6	330/679
Uranium Hexafluoride	UF_6	330
Vinyl Bromide	C_2H_3Br	320/510
Vinyl Chloride	C_2H_3Cl	290/510
Vinyl Fluoride	C_2H_3F	320/350
Vinyl Methyl Ether	$C_2H_3OCH_3$	290/510
Xenon	Xe	580/677
Xenon (Research Grade)	---	590

Appendix M: Hot Plate Safety

The CCE Division Safety Committee recommends the following guidelines for hot plate usage.

Factors which contribute to fires associated with usage of hot plates include:

- Improper use of equipment
- Unattended reactions
- Poor housekeeping practices in fume hoods

A. Equipment

1. Use a temperature control unit or a thermometer to monitor the temperature. Do not use mercury thermometers – instead use an alcohol thermometer.
2. Periodically check the hot plate temperature controls using a water bath and thermometer. Replace unreliable or malfunctioning equipment.
3. Use water baths for temperatures up to 70 – 80 °C. Use silicon oil baths at temperatures of 80 – 200 °C. For temperatures above 200 °C, use a wood's melt pot (amalgam) or sand.
4. Use only heat resistant, borosilicate glassware, and check for cracks before heating on a hot plate. Do not place thick-walled glassware, such as filter flasks, or soft-glass bottles and jars on a hot plate.
5. Do not heat a mixture to dryness – the glass may crack unexpectedly.
6. Be careful when removing hot glassware or pouring hot liquids from a hot plate. Use gripping devices such as tongs or silicone rubber heat protectors.
7. Use a medium high setting of the hot plate to heat most liquids, including water. Do not use a high setting to heat low boiling point liquids.
8. Place magnetic or mechanical stir bars in liquids being heated to facilitate even heating and boiling.

B. Unattended reactions

1. Do not leave a standard hot plate unattended.
2. If a reaction must be left unattended, use a hot plate with overshoot protection.
3. Periodically check the bath temperature.

C. Housekeeping

1. Maintain a three-inch clearance of any materials from a hot plate.
2. Remove any flammable or combustible materials from the fume hood when using the hot plate.
3. Keep the fume hood and work area clutter free.

Appendix N: Vacuum System Safety

A vacuum system is a common piece of equipment found and used in most labs. The main components of a vacuum system include:

- Vessel or system to which vacuum will be applied
- Vacuum gauge
- Trap
- Aspirator or vacuum pump
- Exhaust system

Vacuum systems require special work procedures to reduce the likelihood of the implosion of evacuated glassware that could eject flying glass and chemical. Vacuum work involving hazardous and flammable liquids must be conducted in a fume hood or glove box.

Systems under vacuum pose severe implosion hazards from flying glass shrapnel released during an implosion. Other hazards may include:

- The toxicity of the chemicals in the vacuum system
- Fire following breakage of a flask containing flammable solvents
- Toxicity from the mercury in manometers and gauges
- Over- or under-pressurization arising with thermal conductivity gauges
- Electric shock with hot cathode ionization systems.

A. Vacuum pumps

Before any operation is performed an appropriate vacuum system should be selected.

Type of Vacuum System	Distillation/ Concentration
Mechanical Vacuum Pumps or Facility Vacuum System	▪ Only for less-volatile substances ▪ Removal of final traces of solvents ▪ With suitable trap
Water Aspirator	▪ With suitable trap
Steam Aspirator	▪ With suitable trap

1. Distillations or concentration operations that involve significant quantities of volatile substances should normally be performed with the use of a water aspirator, steam aspirator, or dry pump. Distillation of less-volatile substances, removal of final traces of solvents, and some other operations that require pressures lower than those obtainable with a water aspirator are normally performed with a mechanical vacuum pump. Vacuum pumps should not be used with highly flammable or corrosive substances.

2. Always use a cold trap to collect volatile substances from the system and to minimize the amount of material that enters the vacuum pump and dissolves in the pump oil. A cold trap should also be used with a water aspirator to minimize contamination of discharged water.

3. Do not operate pumps near containers of flammable chemicals.

4. The possibility that mercury will be swept into the pump as a result of a sudden loss of vacuum can be minimized by placing a trap in the line to the pump. Vacuum pump oil contaminated with mercury must be treated as hazardous waste.

5. The output of each pump should be vented to an air exhaust system. This procedure is essential when the pump is being used to evacuate a system containing a volatile toxic or corrosive substance. Although material is usually trapped before the pump, failure to observe this precaution would result in pumping any of the substance that is not trapped into the laboratory atmosphere. Even with this precaution, however, volatile toxic or corrosive substances may accumulate in the pump oil and, thus, be discharged into the laboratory atmosphere during future pump use. When it becomes contaminated, make sure to drain and replace the pump oil. The contaminated pump oil should be disposed of by following standard procedures for the safe disposal of toxic or corrosive substances. General-purpose laboratory vacuum pumps should have a record of use in order to prevent cross-contamination or reactive chemical incompatibility problems.

6. Belt-driven mechanical pumps with exposed belts must have protective guards. Before using the vacuum pump, ensure that the moving parts have been properly guarded and that there are no exposed points of operation (i.e., exposed belt) that could nip a finger or catch hair or clothing. Ensure that service cords and switches are free from defects. Wear eye protection when working with a vacuum pump or setting up the cold trap assembly.

B. Cold trap

A cold trap is a condensing device to prevent moisture contamination in a vacuum line. A cold trap should be fitted on the suction line when working with volatile substances in a vacuum system. This will minimize the amount of material that enters the discharge water or pump oil. The recommended cold trap coolant is a mixture of dry ice and isopropyl alcohol. Additional filters may be needed to prevent release of particle matter.

Guidelines for using a cold trap include:

1. Locate the cold trap between the system and vacuum pump.
2. Ensure that the cold trap is of sufficient size and cold enough to condense vapors present in the system.
3. Check frequently for blockages in the cold trap.
4. Use isopropanol/dry ice or ethanol/dry ice instead of acetone/dry ice to create a cold trap. Isopropanol and ethanol are cheaper, less toxic, and less prone to foam. Neither acetone nor ether is recommended, due to volatility and flammability.
5. Do not use dry ice or liquefied gas refrigerant bath as a closed system. These can create uncontrolled and dangerously high pressures.
6. Liquid nitrogen, a cryogenic, should not be used as a coolant since liquid oxygen can concentrate in the trap, inviting explosion. When using liquid nitrogen, care must be taken to avoid the formation of liquid oxygen in cold-traps that are open to air or the increase of liquid oxygen content in a flask of liquid nitrogen that has been cold for a long period. (Liquid oxygen has a blue water-like appearance). Solid carbon dioxide (dry ice) should be considered as an alternative coolant in situations where liquid oxygen could accumulate. If a cryogenic must be used as a coolant, consult with your laboratory supervisor and refer to Appendix H “Vacuum Transfers” of the CCE Division Chemical Safety Manual http://www.cce.caltech.edu/resources/Safety2.pdf

C. Capture of contaminants

1. Each vacuum system used for solvent distillation operations is protected by a suitable trapping device (cold trap, filter, liquid trap) with a backflow check valve.
2. Water, highly flammable solvents, and corrosive gases should not allowed to be

drawn into the vacuum system.

3. When mechanical vacuum pumps are used with volatile substances, the input line to the pump is fitted with a cold trap to minimize the amount of volatile materials entering the pump and dissolving in the oil.

4. If particulates could contaminate a vacuum line (e.g., from an inert atmosphere dry box or glovebox), a HEPA filter will be installed.

5. If pump oil becomes contaminated with toxic chemicals, it will exhaust the chemicals into the room air during future use. Pump oil shall be changed if it becomes contaminated. Dispose of used pump oil with ORS.

6. The exhaust from evacuation of volatile, toxic, or corrosive materials is vented to an air exhaust system such as a chemical fume hood or local exhaust duct.

D. Vessels

Vessels used in vacuum operations should be protected with suitable relief valves (vacuum breaker). A protective shield should placed around evacuated systems. The glassware used with vacuum operations must meet the following requirements:

1. Only heavy-walled round-bottomed glassware should be used for vacuum operations. The only exception to this rule is glassware specifically designed for vacuum operations, such as an Erlenmeyer filtration flask.

2. Carefully inspect vacuum glassware before and after each use. Discard any glass that is chipped, scratched, broken, or otherwise stressed.

3. Wrap exposed glass with tape to prevent flying glass if an implosion occurs.

4. Dewar flasks are wrapped with tape or enclosed in wooden or metal containers.

5. Vacuum desiccators are made of borosilicate/Pyrex glass or plastic. Evacuated desiccators should never be carried or moved. Wait to open desiccators until atmospheric pressure has been restored.
6. If rotary evaporators are used, increases in rotation speed and application of vacuum to the flask are gradual.

E. Vacuum Gauges

The type of vacuum gauge to be used is determined by the pressure range to be measured. The vacuum gauge should be placed in the system close to the test vessel between the trap and vessel.

F. Vacuum Work Procedures

1. Wear personal protective equipment including explosion shield and face shield.
2. Work in a fume hood.
3. Select appropriate vacuum system:
4. Water aspirator if using solvents or corrosive gases.
5. Install a solvent collection device and a trap with a check valve between the water aspirator and the apparatus to prevent water from being drawn back into the apparatus
6. When using a mechanical vacuum pump:
7. Use a cold trap
8. Vent to an fume hood or exhaust system to the outside of the building
9. Belt driven mechanical pumps with exposed belts must have protective guards

If solvents or corrosive substances are inadvertently drawn into the pump, the contaminated oil should be immediately changed and disposed of as hazardous waste.

Appendix O: NMR Magnet Safety

An NMR magnet is always on. NMR magnets have very strong, static magnetic fields. Magnet strength is normally described in terms of Gauss or Tesla units. (1 T = 10,000 G). Typical strengths are as follows:

Earth's magnetic field:	0.6 Gauss at equator
Refrigerator magnet:	100 to 150 Gauss
MRI medical scanners:	0.3 to 1.5 Tesla (3,000 to 15,000 G)
High field NMR magnet:	
200 MHz:	4.7 Tesla (47,000 G)
300 MHz:	7.0 Tesla (70,000 G)
500 MHz:	11.7 Tesla (117,000 G)
800 MHz:	18.8 Tesla (188,000 G)

The strengths listed above are the strength of the magnet at its center (inside the bore where the sample is placed). The magnet field strength falls off as you move away from the magnet center. The rate at which it decreases depends on the physical size and geometry of the magnet. For example, the wider the magnet bore, the further out the magnetic field lines will extend and the stronger the magnetic field that will be felt by nearby magnetic objects.

5 Gauss Region:

For most purposes, you only need to know the location where the magnetic field strength drops to 5 Gauss. Signs, plastic chains, and/or marks on the floor mark the location of the 5 Gauss field line around each NMR magnet.

The magnetic field inside the 5 Gauss region can cause damage to medical implants and pacemakers.

DO NOT ENTER THE 5 GAUSS REGION IF YOU HAVE ANY MEDICAL IMPLANTS WITHOUT APPROVAL OF YOUR PHYSICIAN.

10 Gauss region:

The location of the 10 Gauss region is located slightly inside the 5 Gauss region. At this field strength, watches, credit cards, and other personal items can be damaged. More importantly, NO tools or metallic objects should be taken closer to the magnet than this point.

Metal objects can be attracted to the magnet causing flying metal projectiles. Ferromagnetic objects can reach speed approaching 45 mph entering the bore of the magnet. One cannot react fast enough to hold on to an object once it is accelerated in the magnetic field.

These objects can cause personal injury or death if there is anyone between them and the center of the magnet. If the objects strike the magnet they can distort magnet’s wires or internal dewars and/or become lodged inside the magnet bore. This can cause the magnet to quench.

Appendix P: High Pressure and Vacuum Work

Pressure differences between equipment and the atmosphere result in many lab accidents. Glass vessels under vacuum or pressure can implode or explode, resulting in cuts from projectiles and splashes to the skin and eyes. Glass can rupture even under small pressure differences. Rapid temperature changes, such as those that occur when removing containers from liquid cryogenics, can lead to pressure differences, as can carrying out chemical reactions inside sealed containers.

The hazards associated with pressure work can be reduced by:

- checking for flaws such as cracks, scratches and etching marks before using vacuum apparatus
- using vessels specifically designed for vacuum work. Thin-walled or round-bottomed flasks larger than 1 L should never be evacuated
- assembling vacuum apparatus so as to avoid strain. Heavy apparatus should be supported from below as well as by the neck
- taping glass vacuum apparatus to minimize projectiles due to implosion
- using adequate shielding when conducting pressure and vacuum operations
- allowing pressure to return to atmospheric before opening vacuum desiccators or after removal of a sample container from cryogenics
- wearing eye and face protection when handling vacuum or pressure apparatus

Appendix Q: Hazardous Chemical Emissions: Use of Thiols

DIVISION OF CHEMISTRY AND CHEMICAL ENGINEERING MEMO

TO: CCE Division graduate students, postdocs, and faculty
DATE: June 5, 2009
FROM: CCE Division Safety Committee
SUBJECT: Hazardous Chemical Emissions

Recently, a strong chemical odor was released throughout Noyes Laboratory. The odor was identified as a thiol compound, which was released when a researcher used a bench-top rotary evaporator. Upon disassembling the rotovap apparatus on the bench, the strong odor was distributed by the building ventilation system to every floor in the building. Several calls were received from building occupants concerned about their safety.

Any activity performed outside of a fume hood can adversely impact indoor air quality and create a health hazard for the building occupants. Therefore, it is imperative that each chemical procedure be reviewed for its potential impact on indoor air quality. Possible alternatives should be sought that do not generate hazardous emissions. For those circumstances where no alternatives exist, safe mechanical ventilation, such asa fume hood, should be used to remove contaminants from the building, as a means to maintain the health and safety of the occupants.

Thiol compounds must be used carefully and in a fume hood. Care should be taken to use a rotovap placed in the hood. A bleach bath will remove residual odors from glassware, and a small amount of bleach can be added to traps if necessary.

Appendix R: CCE Safety Check-In Sheet

The following sheet is the CCE Safety Check-In Sheet.

The Safety Check-In Form must be completed before building access or a key to any CCE building, lab or office is authorized.

Researchers in Chemistry should bring the completed form to the CCE Division Office in Crellin Lab.

Researchers in Chemical Engineering should bring the completed Form to the Assistant to the Executive Officer for Chemical Engineering in Spalding Lab.

SAFETY CHECK-IN SHEET FOR CHEMISTRY AND CHEMICAL ENGINEERING

Researcher:	____________________	____________________	____________________
	Last Name Printed	***First Name Printed***	***Signature***
Supervisor:	____________________	____________________	____________________
	Last NamePrinted	***Signature***	***Date***

Please check: ☐ Graduate Student ☐ Undergrad ☐ Post Doctoral ☐ Staff ☐ Visitor ☐ Other
Training in Safety is required for everyone in the CCE Division. Before beginning work, each new researcher must have documented training in the following areas. Review the sections indicated below and initial and date when complete.

	Safety Orientation for all, including office staff	Initial	Date
I.	Safety plan for the CCE Division *(page 5)*	______	_________
II.	CCE Division Safety Organization *(page 6)*	______	_________
III.	Hazard Communication Regulations *(pages 8-10)*	______	_________
IV.	Injuries/Illnesses *(pages 11-13)*	______	_________
V.	Safety Equipment *(page 14)*	______	_________
VI.	Emergency Evacuation Assembly Areas *(page 15)*	______	_________
	Laboratory Safety – for researchers in chemical laboratories		
VII.	Viewing Safety Videotapes *(page 16)*	______	_________
VIII.	Electrical Equipment *(page 17)*	______	_________
IX.	Hazardous Waste Disposal *(pages 18-22)*	______	_________
X.	Spill Clean-up *(pages 23-25)*	______	_________
XI.	Responding to an Incident *(page 26)*	______	_________
XII.	Safety Consideration in Work Planning *(pages 27-29)*	______	_________
XIII.	Group Safety Plans *(page 30)*	______	_________
XIV.	General Laboratory Safety Inspection *(page 31)*	______	_________
XV.	Prestart-Up Inspection/Reactive Chemical Program *(pages 32-34)*	______	_________
XVI.	Hazard Identification Diagram *(pages 36-39)*	______	_________
XVII.	Health Hazards of Chemicals *(pages 40-50)*	______	_________
XVIII.	Information Sources for Hazard Evaluation *(pages 51-52)*	______	_________
XIX.	Peroxide-Forming Compounds *(pages 53-57)*	______	_________
XX.	Oxidizing/Explosive/Shock Sensitive Materials *(pages 58-61)*	______	_________
XXI.	Air- or Water-Sensitive Materials (*page 62)*	______	_________

Group Safety – Procedures developed by each research group and topics that are covered in documents other than the CCE Division Chemical Safety Manual.
Consult with your Group Safety Officer*.* ______ _________

Group Safety Officer Signature ______________________________________ Date________________

When complete, return this form to:

Chemistry	**Chemical Engineering**
☐ **Division Office**	☐ **Karen Baumgartner**
(Mail code 164-30, 168 Crellin Lab)	(Mail code 210-41; 204 Spalding Lab)

Rev. 9/1/2013

Appendix S: CCE Laboratory Check Out Sheet

The following sheet is the CCE Laboratory Check Out Sheet

CCE LABORATORY CHECK OUT SHEET

____

Print Full Name of Researcher

CCE Division or Chemical Engineering Administrative Sign Off

☐ Keys returned to CCE Division Office, Chemical Engineering, or Caltech Lock Shop

____

Sign off by CCE Division Office, ChE Admin or Lock Shop, Date

☐ Library Books Sign Off

____

Sign off by Librarian, Date

☐ Forwarding Address of Researcher

____

____

☐ Sign off for either:

Chemical Engineering by the ChE Graduate Option Secretary or
by the Assistant to the ChE Executive Officer, and date

____

or Chemistry by the CCE Division Office, and date

____

Research Laboratory Sign Off

☐ All research samples labeled and in group storage.
☐ All waste materials labeled and moved to waste collection center.
☐ Laboratory bench clean and all chemicals moved to store room.
☐ Laboratory notebook and computer diskettes.
☐ Spectra and other data.

____

Sign off by Group Safety Office or Research Advisor, Date

Return completed form to the CCE Division Office, Mail Code 164-30

Appendix T: Prestart-Up Inspection

Please refer to the Environment, Health, and Safety Office or Joe Drew, the Facilities Coordinator (Ext. 2745).