SAFETY IN THE CHEMICAL LABORATORY

SAFETY MANUAL
DEPARTMENT OF CHEMISTRY
ILLINOIS WESLEYAN UNIVERSITY

Revised by Dr. Mohan (May 2001)

Safety is a very important component of your research career in chemistry. All workers in the laboratory must work in a manner that is in the interest of their safety and that of their co-workers.

This manual includes general guidelines on safe practices for common laboratory operations as well as some more specific hazards in the lab. The manual does not cover all the hazards you are likely to encounter in the lab. Your research advisor will be knowledgeable about specific hazards associated with your work. In addition you can consult the following books for more information:

(1) "*Prudent Practices for Handling Hazardous Chemicals in the Laboratory*" issued by National Research Council and published by National Academy Press.

(2) "*Safety in Working with chemicals*" by Michael Green and Amos Turk, published by Macmillan.

(3) The "*Merck Index*" provides useful information on the physiological properties of many compounds.

Please read this safety manual carefully. You will be then required to take a "safety exam" on your own. The exam will be graded and the results will be returned to your research advisor who will then discuss the exam with you.

Access to the laboratories, stock room and other research facilities is a privilege. Willful or neglectful violations of the safety guidelines will result in loss of your access to these services and facilities.

1. FIRE HAZARDS

A major hazard one can face in the chemical laboratory is that of fires. Please familiarize yourself with the location and types of fire extinguishers and fire alarm pull stations. In the event of a fire, do not put yourself in danger to extinguish the fire.

- If there is a major fire, pull the fire alarm located at the end of the hall. This will alert the campus security who will then alert the local fire department. If you can call security (through the desk at 3034), do so but not at the risk of risk to your self. Do not call the fire department directly unless you are unable to reach security. If it is a small fire you feel you can control, do not pull the fire alarm.

It is important to recognize the various types of fires and methods to extinguish them.

Class A Fires: Combustible solids, paper, rubber, plastics. Combustion can result in release of toxic gases.

The most convenient method is to use water. Can also use dry chemical extinguisher, and CO_2 but these result in spreading of the ash over a large area.

Class B Fires: Solvent fires.

These pose the greatest risk, especially in the organic chemistry lab. A measure of the flammability of the liquid is given by "flash point" which is defined as the temperature at which a liquid gives rise to ignitable vapors. Any liquid with a flash point < 15 °C should be regarded as dangerously flammable.

Table 1.

Flash Point of Common Solvents:

Pentane	– 49 °C	Ethyl acetate	– 4.4 °C
Diethyl ether	– 45 °C	Toluene	4 °C
Carbon disulfide	– 30 °C	Acetonitrile	6 °C
Hexane	– 23 °C	Methanol	7 °C
Acetone	– 18 °C	1,4-dioxane	12 °C
Tetrahydrofuran	– 17 °C	Ethanol	12 °C

Carbon disulfide has the very low auto ignition point of 100 °C. The vapors can ignite up on contact with a hot water bath !! Avoid use of CS_2 !

If the fire is contained in a beaker or a small vessel, it can often be extinguished by covering the vessel with a wire gauze or addition of sand or dry ice. If the fire is in a larger vessel or has spread, dry ice is very effective. Dry chemical extinguisher is also useful. CO_2 extinguishers

produce a jet of foam which can result in overturning of the vessel and sometimes aid in spreading of the fire !
Water should not be used for solvent fires.

Class C Fires: Electrical equipment:

Never use water for these fires even if the main is turned off. Many equipment store charge. If power cannot be turned off, dry chemical or inert gas must be used.

Class D Fires: Metal (K, Na, Mg, Li, Al) and Metal hydrides (NaH, KH, $LiAlH_4$, etc)

These fires cannot be extinguished using water, CO_2 or volatile hydrocarbons. Inert powder (sand or talc) must be used. It is best to use Metal X extinguishers.

Some Common Fire Sources In the Lab:

A. Open Flames: Open flames should almost never be used in the lab, especially in the organic chemistry lab. If a Bunsen burner is used, it should be turned off when not in use.

B. Sparks: Volatile and flammable solvents should not stored in open containers nears sources of sparks which include vacuum pumps, drying ovens, thermostats etc.

C. Oxygen cylinders: A leaking oxygen cylinder can lead to an increase in oxygen concentration in the atmosphere which will cause a dangerous fire if a flammable substance and a ignition source are present. All compressed oxygen cylinders should be checked for leaks periodically.

D. Sodium residues: Sodium residue should never be destroyed by addition of water: even if there is only very small quantities. Large quantities are best destroyed by slow addition of 2-propanol to the sodium contained in a round-bottomed flask equipped with a water cooled reflux condenser. Smaller quantities (1-2 g) can be destroyed by very cautious addition of methanol using a similar set-up.

E. Organometallics: These pose a serious fire risk. They must always be handled in an inert atmosphere.

2. EXPLOSIONS

Explosions are usually accompanied by fire or vice-versa ! In addition to fires, there are many chemicals which can lead to an explosion when handled improperly. Some specific dangers of explosions are listed below:

A. Peroxides in ether solvents:

One of the most common cause of explosion in the organic lab is peroxides. Many a laboratory has been destroyed by this ! Simple dialkyl ethers as well as cyclic ethers such a 1,4-dioxane and tetrahydrofuran form less volatile peroxides when exposed to air and light. When these solvents are distilled, the pot residue is enriched in the peroxide and eventually a violent explosion can result. To avoid this risk:

(i) such solvents should not be stored for long in half empty containers.

(ii) it is best to buy smaller containers of ether rather than buy larger containers (which are less expensive) and store for prolonged periods.

(iii) it is best not to distill these solvents when old. But if distillation must be carried out, test for peroxide before distilling. If peroxides are detected, they must be destroyed. The process of drying these solvents with sodium metal usually destroys any peroxides but it is best to discard very old bottles (> 1 year).

B. Alkali metals with halogenated solvents: Alkali metals (Na, K, Li) and also finely divided Al and Mg react violently with halogenated organic solvents especially carbon tetrachloride. **Residues of these metals should never be washed with halogentated solvents.** A dangerous explosion can result.

C. Perchloric acid: This acid reacts violently with most organic material such a rubber, cork, wood etc. Never store perchloric acid near organic material or in a wooden cabinet.

D. Chromic acid and Nitric Acid: These should never be heated with an organic compound. If tarry residues cannot be removed by small quantities of cold chromic acid, the flask is best discarded ! A very dangerous explosion will result if nitric acid is added to alcohols, especially ethanol and methanol.

E. Liquid Nitrogen: Liquid nitrogen (bp – 196 °C) contains some liquid oxygen (bp – 183 °C). When liquid nitrogen evaporates, the residue is enriched in oxygen which can cause an explosion when in contact with an organic substance. It is better to use dry-ice/isopropanol baths rather than liquid nitrogen. If liquid nitrogen is used in traps for vacuum work, it will often cool oxygen from air in the trap. If an organic material is then condensed in that trap, an explosion can result during evaporation. The use of liquid nitrogen in routine organic work is best avoided.

F. Vacuum Work: Before evacuating any glassware, check carefully for cracks. All dewars and rotovap assemblies should be covered with a safety net to prevent flying glass. Vacuum desiccators should be similarly covered.

G. Opening Sealed bottles and Ampoules: Volatile chemicals must be cooled thoroughly before opening. Cooling should be done in steps, not rapidly. A salt-ice bath is usually sufficient for most purposes.

H. Compressed gas cylinders: These should always be secured to a wall. The valves and screws should never be greased. Cylinders should be moved around only in trolleys to which they should be secured. An empty cylinder should be immediately labeled clearly.

3. Some Dangerous Inorganic Chemicals:

Strong Acids:

All of the following give off very harmful vapors and also react violently with bases. They should always be handled with gloves and in the hood. Adequate eye protection must also be worn.

- Hydrobromic acid and HBr gas
- Hydrochloric acid and HCl gas
- Hydrofluoric acid and HF gas— Both react with glass ! Rubber or plastic gloves should be worn. Skin burns require immediate medical attention.
- Nitric acid and Perchloric Acid (See under Explosions Section)
- Sulfuric acid: caution must be exercised when diluting this acid. Always add acid to water slowly with stirring. Never the other way around.

Strong Bases:

Most inorganic bases have a very corrosive action on the corneal tissue of the eye. Hence safety glasses are particularly important when handling these compounds. Solutions of alkalis tend to bump when heated. Exercise great care when heating these. Use a stir bar to insure smooth heating.

Halogens:

The most common halogen in the lab is perhaps bromine. Glassware containing bromine residue must be never rinsed with acetone since this results in the formation of the powerful lachrymator, bromoacetone. Instead, destroy residual aqueous bromine by addition of a solution of sodium metabisulfite in water (10 % aq. solution). Since this results in production of SO_2 gas, this process must be done in the hood. Bromine in carbon tetrachloride or other organic solvents can be destroyed by adding cyclohexene and then disposing the mixture in a container for halogenated waste.

Reactive halides:

Boron tribromide, boron trichloride, aluminum chloride, phosphorous trichloride, phosphorous pentachloride and phosphorous oxychloride etc., are very reactive toward water. They should not be exposed to air for any length of time as they will release toxic gases.

4. CHEMICAL HAZARDS:

Given below is a list of some dangerous chemicals that are often encountered in the lab. This is not a complete list of such chemicals ! It simply inludes the more common reagents. Many of these are useful compounds. While their useful properties should be taken advantage of, it is important to be aware of the risks so that adequate precautions can be taken while handling them.

The following are severe lachrymators (cause copius watering of the eyes)

acetyl chloride
acrolein
allyl alcohol
allyl chloride
benzyl chloride
diketen
dimethyl acetylenedicarboxylate
benzoyl chloride
bromoacetone (easily produced by mixing bromine with acetone)
oxalyl chloride

The following are a major explosion hazard especially when heated:

- sodium azide
- diazomethane
- acetylene salts
- p-toluenesulfonyl azide
- diazonium salts
- perchlorates

The following are extremely toxic by ingestion and can be fatal in even small doses:

- aromatic amines (aniline and its substituted derivatives)
- arsenic and its compounds
- hydrogen sulfide (this gas with the odor of rotten eggs cannot be detected at higher concentrations !)
- mercury chloride
- nitric oxide and nitrogen dioxide
- osmium tetroxide (severe hazard to eye)
- oxalic acid and its salts
- phenols and aromatic nitro compounds
- selenium and its compounds
- sodium and potassium cyanide
- thallium acetate and other thallium salts
- vanadium pentoxide

The following substances have very harmful cumulative effects which manifest after prolonged exposure over a relatively long period. If you will be working with these for long periods of time, biological monitoring of the body may be necessary.

- benzene (it has a mildly pleasant odor; if you can smell it, you are inhaling dangerous quantities)
- isocyanates (in particular toluene isocyanate)
- lead and its compounds
- mercury and mercury compounds

The following are known or suspected carcingoens. If you must use these, make every effort to wear gloves, handle them only in the hood and wear protective clothing. Label all vials and flasks containing these appropriately

Amines

1,1-dimethylhydrazine
hydrazine
methyl hydrazine
1- and 2-napthylamines

Nitroso compounds

All nitroso compounds are potential carcinogens.

Alkylating agents

aziridine
Bis(chloromethyl) ether
diazomethane
epichlorohydrin
methyl iodide
propiolactone

Aromatic hydrocarbons

benzene
benzo[a]pyrene
dibenz[a,h]anthracene
7,12-dimethylbenz[a]anthracene

Halogenated hydrocarbons

carbon tetrachloride
chloroform
1,2-dibromoethane
hexachlorobutadiene
vinyl chloride

Phosphorous and Sulfur compounds:

hexamethylphosphoramide
1,3-propanesultone (3-hydroxy-1-propanesulfonic acid)
thioacetamide and thiourea

5. The following section discusses safety aspects associated with some common lab procedures:

1. The following statements concern the use of a rotary evaporator:

(a) The body of a rotovap should not be protected with a safety net since this can obscure the vision of the condenser and the condensates. Say True or false.

This is false. Implosion is a serious hazard. Safety net does not obscure vision. The risk from an implosion is real and dangerous.

(b) What is the largest size flask that should be used in most rotovaps ?

One liter flask.

(c) Can a Erlenmeyer flask be evacuated ?

No, Flat surfaces vessels should never be evacuated unless they are specifically designed for the purpose (such as filtration flasks)

(d) Is there a greater risk in evacuating a rotovap with a vacuum pump (<0.5 mm Hg) than with a water aspirator (20 mm Hg?

No. the risk is the same. Both pressures are quite far from atmospheric pressure. It is the pressure differential that is important.

2. Why should contact lenses be never worn in the laboratory ?

Soft contact lenses will absorb organic vapors like methanol, chloroform etc. If chemicals enter the eye, then eye cannot be easily washed due to contact coverage. Only ANSI-Z87.1 approved safety glasses must be worn in the laboratory.

3. Familiarize yourself with the location of fire extinguishers, first-aid boxes and circuit breaker boxes (in the event that power has to be shut off) for the labs that you will be working in.

4. Suggest best ways to dry the following solvents:

Diethyl ether and tetrahydrofuran: These are best dried with sodium metal. Even though the use of Lithium aluminum hydride (LAH) has been recommended and is often used in many

research groups, **LAH should not be used to dry ethers**. LAH decomposes (often explosively) at 125 °C, a temperature that can be easily attained with a heating mantle.

Dichloromethane and acetonitrile: Calcium hydride

Methanol and ethanol: Magnesium metal (caution: the reaction is vigorous)

5. What is the best solvent for use in cooling baths containing dry-ice ?

Isopropyl alcohol is the preferred solvent. Acetone is commonly used but is more flammable and hence its use should be avoided in cooling baths.

6. One of the most common accident in a lab results from broken glass. What precautions can be taken to avoid such injury ?

Broken glassware should either be repaired immediately or disposed off in the appropriate container. They should never be left around. Never force glass tubing through a rubber cork. Always lubricate cork and glass tubing with glycerin. Wear leather or thick rubber gloves when inserting tubing through corks etc.

7. What is the best way to heat flasks and round bottomed flasks containing flammable liquids ?

An oil bath provides good temperature control. Heating mantels should be avoided since they do not provide good temperature control. A temperature controller (if available) should be attached to the oil bath.

8. The building ventilation in the Science wing is supposed to be good. This will result in a lower internal pressure than the pressure outside. As a consequence, odors and toxic gases can be swept back into the lab through open sinks. So never pour solutions of thiols, HCN etc. down the drain.

9. Unlabeled chemicals pose a great hazard. Current US Environmental Protection Agency regulations forbid disposal of unknown chemicals. How should unlabeled chemicals be handled ?

Sometimes identification is easy (A ^{1}H NMR might reveal the nature of the compound). Often partial labels can be found on bottles. Look for hazard symbols such as flammable, explosive etc. Do not add water or other chemicals to unknown reagents in an attempt to destroy them till their identity is established and you are certain that they can be destroyed safely.

10. Describe the appropriate clothing that must be worn in a lab.

Loose clothing should never be worn in the lab. They pose a greater fire hazard. Long hair also poses a similar risk. Shorts and sleeveless dress offer less protection than long pants and full sleeve shirts. If a corrosive chemical is being handled, it is best to wear a laboratory coat. Shoes must be worn at all times in the lab. Open toed shoes and sandals offer little protection against spills and hence are not permitted in the lab. Hosiery should not be worn since they "melt" upon contact with acids.

11. The following section describes the use of gloves.

Leather gloves are best for handling broken glass and for inserting tubing into corks but they do not offer protection from chemicals.

There are many kinds of gloves available in the market. Check with your research advisor to see if a particular kind is more suited for the type of work you are doing. Latex surgical gloves are of little value in the chemical laboratory and should not be worn. It is important not to spread chemicals and spills with gloves: Do not handle door knobs, items in stock rooms and instruments with contaminated gloves.

12. When should a blast shield be used ?

Whenever a potentially explosive reaction is being carried out (such as generation of diazomethane) or the use of a pressurized equipment is involved, a safety shield should be used to provide added protection against an implosion.

13. When should the safety shower be used ?

It is unlikely that you will ever need to use one. But in the event of a major spill on your face, neck, eyes, head or shoulders, use the safety shower immediately. Do not worry about being modest ! Contaminated clothing should be immediately removed. Hence it is a good idea to have lab coats available in every lab !

14. What are the five hazard classes recommended by Environmental and Safety for separating chemicals ?

Flammables
Oxidizers
Acids
bases
Reactives

15. How should glass bottles containing solvents be carried around in the hallways ?

A bottle carrier should always be used in the halls, elevators and stairwells.

16. What is the best container to collect waste solvents ?

The EPA requires that waste solvents be collected in polyethylene jerri cans. Metal cans rust easily while glass bottles are easily broken.

17. Flooding: Major damage to equipment has often resulted from flooding. How can this be avoided ?

- **Do not use tubing that is too old or brittle.**
- **Don't use pure gum rubber tubing for water lines**
- **All tubing must be secured with wire or clamps.**
- **Unattended water lines must have a regulator.**
- **Check sink for debris that can clog the sink and cause water to back up.**

18. What should I do if there is a mercury spill (as is common when a thermometer breaks) ? How can this be avoided ?

- **A catch pan must be provided under all mercury containing equipment (such as manometers and McLeod Gauges).**
- **Use a non-mercury thermometer whenever possible.**
- **Never use a Mercury thermometer in a heated oven**
- **The use of sulfur has been recommended but it is unclear whether this serves any purpose. (It is believed that this lowers the vapor pressure). It is best to remove the mercury than spray sulfur all over !**

19. What common substance can react explosively with Teflon (there are many Teflon objects in the lab such as stirrers, tubing etc.) at high temperatures ?

Potassium metal

20. In the event of "small" spill, describe the steps you will take to insure a smooth and complete clean up.

- **<u>Personal Safety:</u> Wear appropriate clothing and eye protection. Wear gloves.**

- **<u>Containment of spill:</u> Turn off sources of ignition such as burners if a flammable material is involved. Do not turn light switches off or on as that can generate a spark. Close all lab doors to contain the spill.**

- **<u>Absorb the spill:</u> Absorb the spill with a spill absorbent.**

- **<u>Cleanup:</u> Scoop he mixture into a plastic bag and label appropriately. Turn it into the stock room and fill up a waste disposal form.**

21. What special precautions must be observed when running overnight reactions or reactions that have to be left unattended for some length of time ?

- **An index card containing the following information should be posted clearly outside the hood or near the reaction site.**

- Your name and telephone contact number

- Contents of the flask. This is useful if someone else has to respond to an emergency situation associated with your reaction.

- If water is being used through a hose, make sure it is secured with hose clamps. Also insure that the sink is <u>not</u> clogged with debris.

- Oil baths should not be heated overnight unless a temperature controller is installed in the bath.

<u>WHAT TO DO IN CASE OF A MAJOR FIRE ?</u>

PULL THE FIRE ALARM AND EVACUATE THE BUILDING IMMEDIATELY. DO NOT PUT YOUR LIFE IN JEOPARDY.

<u>WHAT TO DO IN CASE OF A MAJOR ACCIDENT THAT SEEMS LIFE THREATENING (SUCH AS A SEVERE CUT OR A CHEMICAL BURN)</u> ?

- **IF THE ACCIDENT INVOLVES YOUR LAB MATE OR SOMEONE AROUND YOU, KEEP THEM CALM. CALL CAMPUS SECURITY THROUGH THE PHONE IN THE HALLWAY (DIAL 3034 TO REACH MEMORIAL DESK WHO WILL PUT YOU THROUGH TO SECURITY). IF THERE IS NO IMMEDIATE RESPONSE, CALL 911 BY DIALING 9-911. DO NOT HANG UP TILL THEY HAVE THE**

NECESSARY INFORMATION. TELL THEM YOU ARE IN THE SCIENCE BUILDING OF ILLINOIS WESLEYAN UNIVERSITY ON E. BEECHER STREET.

- **You should <u>not</u> be working alone in the lab. If at the moment of the accident there is no one in your vicinity, call for help by screaming ! If you can make it to the phone, dial 3034. Stay calm. If it is a burn, keep injured body part under cold water.**

- **DO NOT ATTEMPT TO MOVE THE INJURED PERSON. KEEP THEM CALM. THE ONLY EXCEPTION TO THIS IS IF THE ACCIDENT ALSO INVOLVES A FIRE.**