TOWSON UNIVERSITY

Chemical Safety
Chemical Hygiene Program

Procedures for the Safe Storage of Chemicals
Manual

Department of Environmental Health & Safety

Phone:	(410) 704-2949
Fax:	(410) 704-2993
Email:	safety@towson.edu
Website:	https://www.towson.edu/public-safety/environmental-health-safety/
Emergency:	911
TUPD:	(410) 704-4444

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Purpose

The purpose of this procedure is to establish rules for the safe storage of chemicals on campus.

Scope

The scope of the procedure pertains to the labeling and storage of chemicals by University faculty/staff. The procedure primarily applies to laboratory chemicals, which for the purposes of laboratory use are stored in portable containers in volumes of less than or equal to five (5) gallons. This procedure does not directly apply to compressed gas cylinders/tanks.

Definitions

CIDB: Chemical Inventory Database program related to tracking chemical inventory and safety data sheets. The computer application, Vertere ChIM, is used to administer the program.
Hazard Materials Identification System (HMIS): A labeling system used to detail chemical hazards and appropriate personal protective equipment to use.
National Fire Protection Association (NFPA): An organization that creates industry standards to reduce fire hazards and provides information about chemical hazards.

Responsibilities

- **A. Environmental Health & Safety (EHS)**
  1. EHS will assist in spill cleanup, decontamination, and disposal as required.
  2. EHS will provide safety training and information as required.
- **B. Deans, Department Heads, and Principal Investigators** (Supervisors)
  1. Supervisors will assign/provide appropriate space and equipment for storage.
  2. Supervisors will ensure that laboratory personnel are in compliance, properly labeling and storing chemicals.
- **C. Laboratory Personnel**
  1. Laboratory personnel will follow procedures contained herein, by properly labeling and storing chemicals.

Introduction

The safe storage of chemicals is important to avoid injuries, illness, or worse health outcomes. There are additional concerns such as equipment/property damage, product loss, and loss of funding, and time. Storage issues include accidental exposures to chemical hazards; leaks or spills which may lead to slips, trips, falls, or property damage; hazards from equipment that may lead to injuries or property damage; and fires. The causes may be due to faulty storage equipment; facility failure; ambient conditions; stockpiling; container rupture/failure due to age, impact, or other activity; container not being tightly sealed; container improperly labeled; chemical incompatibilities or accidental mixing; other improper storage; instability that is characteristic to specific chemicals; or a lack of awareness/training. The procedures described herein will assist in avoiding perils in chemical storage.

Applicable Regulations

- 29 CFR 1910.1200 – Hazard Communication
- 29 CFR 1910.1450 - Occupational Exposure to Hazardous Chemicals in Laboratories

Procedure

A. **Inventory Practices & Inspection**

1. It is the responsibility of the Instructors/Principal Investigators (PIs) to ensure that chemicals are stored properly in each laboratory and that there is a current written/electronic inventory of all stored chemicals.
2. This inventory should be stored in a central location outside of the laboratory or available online (CIDB), and it must be immediately accessible to emergency responders at all times.
3. The inventory should include, but not be limited to, the chemical name and on-hand quantity.
5. Each chemical should be labeled properly, have a designated storage place, and should be returned to that place after each use.
   a) Container labels must be present, legible, and intact.
   b) Do not remove or deface any existing labels on incoming containers of chemicals. Most manufacturers will meet current labeling requirements.
   c) If labels are damaged, missing, or illegible, the label must be replaced.
   d) If a chemical is repackaged into a new container, label requirements must be met for the new container or add essential information from the old container.
   e) If the item is experimental, the researcher's name and any sample identification should be part of any label.
   f) As a general rule of thumb, it is a good practice to date all chemical containers when first received with the following information to avoid the retention of expired or off-specification chemicals and to ensure the timely disposal of potentially reactive chemicals:
      i. Date Received
      ii. Date First Opened
      iii. Date to be Discarded
6. Chemical storage areas should be inspected annually for outdated or unneeded items, illegible labels, leaking containers, etc.
7. Chemicals may be locked in storage containers/area for security purposes, but these areas must be unlocked during inspections.
8. Degradation in storage areas/equipment may suggest improper chemical storage that requires cleaning, repair, and/or removal of chemicals or equipment.
9. Locations that house chemicals shall be kept clean and organized to avoid unnecessary exposures and accidents. Any chemical residues should be cleaned up using the appropriate materials and disposed appropriately.
10. The storage arrangement must be based on hazard class, not the alphabet, and should be posted to show the exact location of the chemical groups.

    a) See Appendix A for guidelines on how to store chemicals.
    b) Section 7 (Handling and Storage) of the safety data sheet (SDS) for the chemical may provide guidance on specific storage conditions that should be met.

11. When chemicals are used, rotate stock so that the oldest containers are used first.
    a) This will help avoid degradation of older chemicals and their containers.
    b) Crystallization, rust/corrosion, bulging, gouging, melting, delamination/peeling, discoloration, cracking, or crumbling for the container cap, label, or body are signs of degradation where the chemical should be removed.

B. Chemical Container Use

1. Use
    a) Always store containers upright.
    b) Containers must be intact to use.
        i. Container integrity prevents chemical escape, property damage, and personnel exposure.
        ii. If the container is damaged, has a missing cap, or is otherwise not feasible to use, contents must be transferred to an intact container, and/or the original container must be removed as waste.
    c) Always check compatibility of the container before dispensing a chemical into it.
    d) Ensure that chemical containers are clean after use. The container cap, label, and body should be clear of any hazardous chemical residue. Use appropriate material to wipe containers and dispose appropriately.
    e) When filling a container, do not fill to the top to allow some space for contents to expand or off-gas as necessary. This helps to prevent a leak or rupture.

2. Proper Sealing
    a) Never store hazardous chemical containers without a cap. Containers carrying chemicals (e.g. beaker) that are in use may be covered with Parafilm or appropriate sealing material, only temporarily, not for permanent storage.
    b) It is very important that containers of highly toxic, highly volatile, malodorous, carcinogenic, or reactive chemicals be tightly sealed to prevent leakage, odors, or reaction with air.
    c) Make sure that caps and other closures are tight on all hazardous chemicals.
        i. Seal containers to prevent escape of corrosive, flammable, or toxic vapors.

        - ii. *An exception is bottles of waste, such as acid-organic mixtures that may generate gas pressure sufficient to burst a tightly sealed bottle.*
            - 1) *In this case, use an appropriate vented cap that will allow excess gas to be released.*
            - 2) *A vessel of this type should be safely stored in vented storage cabinet.*
    - d) The best seal is the screw-cap with a conical polyethylene or Teflon insert. The caps can then be sealed with tape or Parafilm "M" as a further precaution.
    - e) Additional protection can include the following:
        - i. *Wrapping in an absorbent paper and sealing inside a plastic bag; and*
        - ii. *Storing the bag inside a metal can with a friction-fitting lid.*

3. <u>Purchase & Storage Considerations Based on Container Size</u>
    - a) Smaller container sizes are considered safer for storage and follow the idea that “less is better”. The real or life-cycle cost of a chemical includes its initial purchase price plus the ultimate disposal costs.
    - b) Smaller chemical container sizes also provide the following advantages:
        - i. *Reduced storage hazards*
        - ii. *Reduced storage space*
        - iii. *Safety in handling smaller quantities*
        - iv. *Reduced losses due to out-of-date chemicals*
        - v. *Minimized cost of disposal of "leftovers”*
    - c) Frequently, it costs many times more than the original purchase price to dispose of leftover chemicals. For example, the cost of waste disposal increases per gallon for non-halogenated solvents, including the weight of the container, for reactives, e.g., sulfides, cyanides, flammable solids. Waste disposal costs are constantly increasing and the best method for reducing waste disposal costs is to reduce the amount of hazardous waste being generated.
    - d) The quantity of chemicals accumulated in the laboratory should be kept at a minimum to reduce the risk of exposures, fires, and waste disposal problems. In general, limit container size to one (1) gallon in the laboratory.
    - e) Larger containers should be kept in chemical storage rooms.

C. Storage Color Codes

1. Most chemical manufacturers include chemical storage information on labels.
2. Some chemical manufacturers use color codes on labels and/or caps to indicate health, physical, and chemical hazards. These colors can be used as a guide for storage groups - store same colors together, segregated from other colors.
3. Some manufacturers use the National Fire Protection Association (NFPA 704) hazard warning diamond symbol, the Hazard Materials Identification System (HMIS) colored rectangle or bar, and some labels use pictograms, all of which are helpful for storage

information. Unfortunately, the color schemes are not always consistent among manufacturers. Under most schemes, colors convey the following message:

Table 1. Storage Color Codes. The table displays colors typically associated with chemical storage by function. The color may be observed on the label border, cap, or other banding.

Color	Hazard Type or Other Description
Red	Fire Hazard and/or Flammables
White	Contact Hazard and/or Corrosive (Acids or Bases)
Blue	Health Hazard and/or Toxic or Poisonous
Yellow	Reactivity Hazard and/or Oxidizers
Green, Gray or Orange	Moderate or Slight Hazard (General Chemical Storage)
Striped or "Stop"	Exceptions within the Same Color Code Labels (Example: Yellow-labeled chemicals are stored apart from striped, yellow-labeled chemicals)

D. Chemical Storage Locations & Types

1. Optimally, incompatible chemicals, such as acids and alkalis, should be stored completely separate from one another to prevent mixing in the event of an accidental spill or release of the materials. Limited storage space within the laboratories, however, may prohibit such prudent practice of chemical segregation and storage.
2. If space is limited, it is permissible to store incompatible chemicals in the same storage cabinet provided that the chemicals are segregated according to their hazard class and stored in adequately sized tubs, trays, or buckets while in the cabinet. These secondary containment devices (SCDs) reduce the chance that incompatible chemicals will inadvertently come in contact with each other.
3. Storing chemicals on the floor should be avoided to reduce the risk of accidents leading to injury, spills, contamination from spills, leaks, or other damage.
    a) Floor storage may obstruct evacuation in case of emergency.
    b) Floor storage may increase personnel exposures including skin contact and inhalation of vapors.
    c) If this cannot be avoided, do not store chemicals on the floor without adequately-sized SCDs.
    d) Adequately-sized containment is defined as sufficient volume to either contain 100% of the volume of the largest stored container or 10% of the total stored volume, whichever is greater.
4. Store containers in a manner to avoid impact, excess physical movement (e.g. vibration), biological activity (e.g. mold, etc.), corrosion, direct sunlight, high relative humidity (>60%), and liquid water exposure.

5. <u>Specific Prohibitions</u>
    a) Never store chemicals in hallways, stairwells, or in any areas generally accessible to the public or subject to temperature extremes.

b) Avoid storing chemicals in an area where they may be easily damaged, leading to a container rupture, leak, spill, and/or emission of odor or gas.
c) Do not store chemicals where they will be exposed to weather, such as the building exterior, roof, or near drains/sanitary sewers.
d) Do not store chemicals in electrical/mechanical rooms or areas where there are obvious electrical or fire hazards.
e) Do not store chemicals on carts or equipment used for transporting goods.
f) Do not store (or transport) chemicals in personal vehicles.
g) Do not store chemicals in drawers, where vapors may become trapped, infrastructure degrades, and containers are spilled, not upright, or become missing/lost. A benchtop spill may leak into the drawer and contact the chemical, which could create an unsafe condition. Depending on the chemical, storing in this manner may be a fire hazard.
h) Do not store chemicals in a manner to emit vapors into, comingle with, or otherwise contact PPE or clothing. This may prematurely degrade the PPE or expose personnel directly to the hazard. Similarly, never store chemicals with or near food/drink meant for human consumption (such items are prohibited in laboratories).
i) Do not store chemicals in or on equipment inappropriate for storage (e.g. office equipment, chairs). For offices, follow office safety guidelines in Steps A9 and B3.
j) Never store chemicals within the given clearance of safety equipment (e.g. within 36 inches for eyewashes/safety showers, electrical panels, and fire extinguishers) or near the ceiling (within 18 inches for sprinklers) to avoid obstruction and for equipment to function appropriately in case of emergency.

6. Specific Locations & Types
   a) Benchtops/Tables
      i. *Storage of chemicals on bench tops is undesirable. Such storage is more vulnerable to accidental breakage by laboratory, housekeeping, and emergency response personnel.*
      ii. *To avoid clutter, restrict chemicals on the benchtop to those in current use.*
      iii. *Some benchtops within a laboratory may resemble tables. Do not store items under such tables.*

   b) Biosafety Cabinet (BSC)
      i. *Chemicals should not be stored in a biosafety cabinet, because they are not designed to remove the hazard from chemical fumes and spills. Its airflow recirculates to the room which may expose personnel to the hazardous fumes/gases.*

   c) Cabinets and Shelves
      i. *If possible, avoid storing chemicals above shoulder height. If chemicals are stored above this height, use a stepstool for access.*

    ii. *Large containers (> 1 gallon), liquids, and corrosives should be stored on lower shelves below eye level.*
    iii. *Ensure that cabinets and shelves are structurally sound and capable of supporting proposed storage capacities and that they are chemically impervious to any spilled liquids.*
    iv. *Do not overcrowd shelves or cabinets.*
    v. *Cabinets under hoods and laboratory benches may be used for storage of chemicals. Under hood storage should be limited to the storage of compatible corrosives.*
    vi. *Cabinets for chemical carcinogens or highly toxic chemicals should be locked.*
    vii. *Chemicals shall not be stored directly on top of, around, or behind on storage cabinets.*
    viii. *Ventilated storage cabinets shall be used near fume hoods. Odoriferous or toxic chemicals may be stored in such a cabinet.*

d) Desiccator Jars or Cabinets
    i. *Desiccator jars and cabinets are useful for storage of air and water reactives, toxics, and malodorous chemicals. In case of especially malodorous compounds (e.g. mercaptans), replace the desiccator material with a vapor adsorber (e.g. charcoal) to control odors.*

e) Environmental Rooms (Cold Rooms, Freezers, Warm Rooms/Incubators)
    i. *Such rooms have closed air-circulation systems and recirculate any leaks and escaped vapors within the chamber.*
    ii. *The refrigeration coils in such rooms are aluminum and subject to damage from corrosive atmospheres.*
    iii. *The electrical systems are designed with vapor-proof lights and duplex outlets, but frequently, they are compromised by extension cords and plug strips.*
    iv. *These rooms are not acceptable for storage of flammables, dry ice, or liquid chemicals. If these chemicals need to be refrigerated, they are to be stored in an approved refrigerator or freezer, rather than a cold box.*
    v. *A warning sign should be posted on the door as shown below in Figure 1.*

DANGER
NOT EXPLOSION PROOF
NOT VENTILATED
GROUND ALL ELECTRICAL EQUIPMENT
DO NOT STORE DRY ICE

Figure 1. Danger Sign for Environmental Room. Illustrated is an example of an acceptable danger sign to be affixed to the entrance of an environmental room to warn of potential storage hazards.

    vi. *Storage of hazardous chemicals in warm room/incubators is prohibited.*

f) Ethanol Room
   i. *The Ethanol Room is a specially designated location within the Science Complex strictly used for the safe storage of tax-free alcohol (ethanol) in bulk. The facility is locked and fireproof/explosion-proof.*
   ii. *There may not be any other chemicals stored in this space.*

g) Explosives and Reactives
   i. *A reactive chemical is defined as any substance which may, in the presence of air, water, shock, friction, static discharge, or contamination release very large and potentially harmful amounts of energy. See Appendix C for additional information.*
   ii. *If you discover, or suspect you have discovered, any old, potentially explosive or reactive chemicals,* ***do not handle them****. Contact EHS immediately at either (410) 704-2949 or at safety@towson.edu. Please include the name of the chemical(s), the quantity (1 x 1-pint, etc.) and its location (SC 0123, under the hood, etc.)*

h) Flammable Liquid Storage
   i. *In general, store flammable liquids in an approved flammable liquids storage cabinet (also known as a flammables cabinet), explosion-proof refrigerator, or other explosion-proof storage.*
   ii. *Fire Codes limit the storage of flammable liquids to 10 gallons in open storage, 25 gallons in safety cans, and 60 gallons in flammable liquid storage cabinets per laboratory unit. These limits are for the total quantities on hand, including chemicals in storage, chemicals in use, and wastes. See Appendix B for additional information regarding the storage of flammable liquids.*
   iii. *Never store flammable or combustible liquids near potential sources of ignition.*

i) Fume Hoods
   i. *Chemicals should not be stored in laboratory chemical fume hoods because they may impede airflow, reducing the effectiveness of the hood.*
   ii. *Only chemicals currently used should be in the fume hood.*

j) Peroxide Forming Chemicals
   i. *Peroxide formation in solvents and reagents has caused many accidents. Every worker must learn to recognize and safely handle peroxidizable compounds.*
   ii. *Peroxides are formed by the reaction of a peroxidizable compound with molecular oxygen through a process called autoxidation or peroxidation.*
   iii. *Peroxidizable compounds are insidious. Under normal storage conditions, they can form and accumulate peroxides, which may explode violently when*

subjected to thermal or mechanical shock. See Appendix D for additional information.

    iv. *If you discover, or suspect you have discovered, any old peroxide forming chemicals,* ***do not handle them****. Contact EHS immediately at either (410) 704-2949 or at safety@towson.edu. Please include the name of the chemical(s), the quantity (1 x 1-pint, etc.) and its location (SC 0123, under the hood, etc.)*

k) Refrigerated Storage (Refrigerator or Freezer Units)

    i. *Flammable solvents that require storage at reduced temperature are to be stored only in refrigerators or freezers designed and UL-approved for the storage of flammable liquids.*
    ii. *"Safety" refrigerators for flammable liquid storage and "explosion-proof" refrigerators are both acceptable. Ordinary domestic refrigerators are not to be used for the storage of flammable liquids because of interior arcing contacts.*
    iii. *Because there is no venting of the interior spaces in refrigerators and freezers, all chemicals should have tightly sealed caps.*
    iv. *Signs should be applied to the doors of chemical refrigerators stating: "NO FOOD, BEVERAGE, OR ICE FOR HUMAN CONSUMPTION", or similar message.*
    v. *Chemicals shall not be stored directly on top of, around, or behind a refrigerator/freezer.*

l) Safes

    i. *Safes should be used for controlled substances with access limited to the researcher.*
    ii. *Such a safe should be double-locked, secured behind at least two separate, differently keyed locks at all times.*
    iii. *The safe should be attached/bolted to the floor or wall.*

m) Sinks

    i. *The storage of chemicals or chemical containers in or near sinks where there may be exposure to water or unrestricted access to drains is strictly prohibited and constitutes a potentially serious violation of Clean Water regulations.*
    ii. *Storage near or under sinks where there may be exposure to water is to be avoided.*

E. Storage by Compatibility

1. At a minimum, always store fuels away from oxidizers.
2. In general, incompatible chemicals in a laboratory should be stored separately where possible, at a distance, in separate cabinets/storage units, or at least separated by secondary containment. Considerations such as vapors mixing or possible leaks should be taken into account.

3. Acceptable Locations
   a) Chemicals should be stored in the laboratory according to their chemical compatibility.
      i. *The diagram Suggested Shelf Storage Pattern in Appendix A indicates a recommended arrangement of chemicals according to compatibility.*
      ii. *These compatibility groups should be stored separately, especially chemicals with an NFPA 704 or HMIS reactive rating of three (3) or higher, and in dedicated labeled cabinets.*
      iii. *Within any compatibility group, chemicals may be arranged alphabetically to facilitate ease of retrieval.*
      iv. *For specific compatibility information for a chemical, consult Section 10 (Stability and Reactivity) of the SDS for the chemical, which may detail dangerous conditions, including storage incompatibilities.*
   b) Chemicals should not be stored in alphabetical order since this practice may place incompatible chemicals next to each other (e.g., sodium cyanide and sulfuric acid) which increases the potential for accidental mixing of incompatible chemicals.

4. The following compatibility groupings are recommended (see Table 2 for examples):
   a) Acids, Inorganic Chemicals
      i. *Store large bottles of acid on low shelves, in special acid cabinets, or cabinets under lab benches.*
      ii. *Place acids in plastic trays for secondary containment in case of breakage, especially glass cleaning solutions of chromic acid.*
      iii. *Segregate inorganic and oxidizing acids from organic compounds including organic acids and other combustible materials.*
      iv. *Segregate nitric acid (>40%) from other inorganic acids.*
      v. *Store acids separate from bases and other reducing agents.*
      vi. *Inorganic salts, except those of heavy metals, may be stored in this group.*
      vii. *Glacial acetic acid should be stored with flammable and combustible materials since it is combustible.*

   b) Bases
      i. *Segregate bases from acids and oxidizers on shelves near the floor.*
      ii. *The preferred storage container for inorganic hydroxides is polyethylene instead of glass.*
      iii. *Place containers in trays for secondary containment in the event of leakage or breaks.*

   c) Organic Chemicals
      i. *Organic compounds should be segregated from inorganics.*

   - ii. *Organics and inorganics with NFPA 704 or HMIS reactive hazard rating of two (2) or less may be stored together.*
   - iii. *Chemicals with a reactive hazard rating of three (3) or four (4) are to be stored separately.*

d) Flammable and Combustible Organic Liquids
   - i. *Fire Codes limit the quantity of flammable and combustible liquids to 10 gallons in open storage and use, 25 gallons in safety cans, and 60 gallons (30 gallons maximum per cabinet with a maximum of 2 cabinets per room) in flammable storage cabinets.*
   - ii. *The materials are to be stored away from sources of ignition such as heat, sparks, or open flames, and are to be segregated from oxidizers.*

e) Inorganic Oxidizers and Salts
   - i. *Store inorganic oxidizers in a cool, dry place away from combustible materials such as zinc, alkaline metals, formic acid, and other reducing agents. Inorganic salts may also be stored in this group.*
   - ii. *Store ammonium nitrate separately.*

f) Organic Peroxides
   - i. *Certain chemicals are shock- or heat-sensitive or become that way during storage. For example, benzoyl peroxide is shock- and heat-sensitive.*
   - ii. *Some chemicals form explosive peroxides or react violently with other chemicals.*
   - iii. *Ethers and other peroxidizable compounds form shock sensitive peroxides in storage.*
   - iv. *Picric acid is classified as a Class A explosive when it contains less than 10% water.*
   - v. *Store shock- and heat-sensitive chemicals in a dedicated cabinet.*

g) Reactives
   - i. *Water Reactives*
     - 1) *Water reactives should be stored in cool, dry place and protected from any water source.*
     - 2) *A Class D fire extinguisher should be available in case of fire.*
     - 3) *As an added precaution, containers should be stored in trays or other secondary containers filled with sand.*
   - ii. *Pyrophoric (Air Reactives)*
     - 1) *Pyrophorics should be stored in a cool, dry place making provision for an air-tight seal.*
     - 2) *White or yellow phosphorous should be stored under water in glass-stoppered bottles inside a metal can for added protection.*

h) Cyanides and Sulfides
   i. *The compounds react with acids to release highly toxic gases. They must be isolated from acids and other oxidizers.*

i) Carcinogenic and Highly Toxic Chemicals
   i. *A dedicated lockable storage cabinet in a "designated area" is the preferred storage method for highly toxic and carcinogenic chemicals. They should be stored in unbreakable, chemically resistant, secondary containers.*
   ii. *The storage cabinet must be posted with a sign stating HIGHLY TOXIC OR CANCER-SUSPECT AGENT.*
   iii. *A separate inventory of all highly acute toxics, carcinogens, and reproductive toxins should also be maintained and accessible to emergency responders. See Appendix E for a listing of potential carcinogens.*

Table 2. Compatible Groups. The table provides examples of chemicals that may be stored together. The group may share similar structures, functionality, and hazards.

Group Name	Chemical Class
Inorganic Acids & Inorganic Salts (Corrosives)	Inorganic acids (except nitric), sulfur, arsenic, halides, sulfates, sulfites, thiosulfates, halogens, phosphorus, phosphates
Inorganic Bases (Corrosives)	Hydroxides, oxides, silicates, carbonates
Organic Chemicals	Alcohols, glycols, amines, amides, hydrocarbons, esters, aldehydes, phenol, cresols, organic sulfides, organic acids
Flammables, Combustibles	Ethers, aliphatic solvents, aromatic solvents
Inorganic Oxidizers	Borates, chromates, manganates, permanganates, chlorates, perchlorates, chlorites, hypochlorites, hydrogen peroxides, amides, nitrates, nitrites, azides
Organic Peroxides	Peroxides, azides, hydroperoxides
Reactives	Air and water reactives, metals, and hydrides
Cyanides, Sulfides	Cyanides, cyanates, sulfides, carbides, nitrides
Poisons & Carcinogens (Toxics)	Severe poisons, carcinogens

5. Alternatively, see Appendix A for Suggested Shelf Storage Pattern for compatible storage groups.

G. Training

1. For training in Chemical Lab Safety, it may be assigned/accessed virtually through Vector Solutions SafeColleges found at the following URL: https://towsonehs-md.safecolleges.com/training/home. Workers shall request training by emailing safety@towson.edu or by calling the Environmental Health & Safety (EHS) office at 410-704-2949.

Resources

A. Handbook of Reactive Chemical Hazards; L. Bretherick, 6th Edition, 1999 (or most current edition)

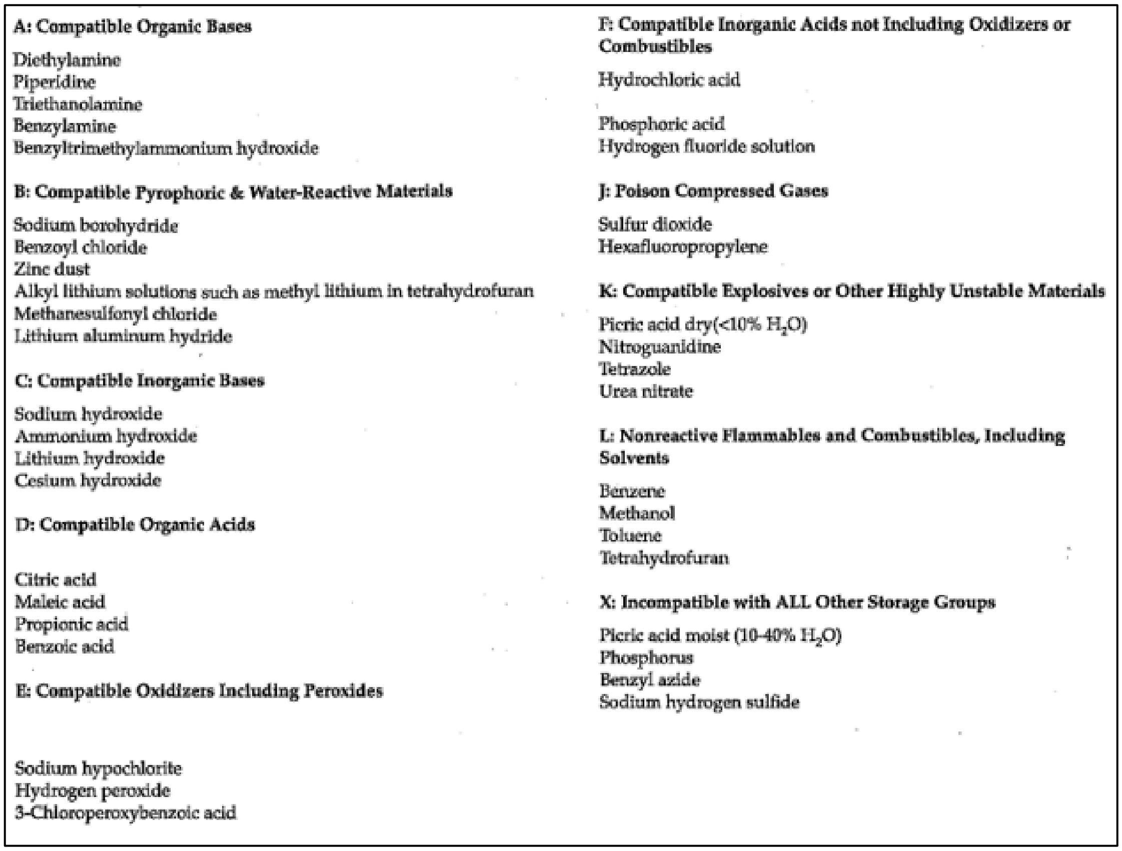
B. Rapid Guide to Chemical Incompatibilities, R. Pohanish and S. Greene, 2nd Edition, 2003 (or most current edition)

C. Prudent Practices in the Laboratory: Handling and Management of Chemical Hazards, National Research Council, 1st edition, 2011 (or most current edition)

D. Environmental Health & Safety

1. To request guidance, training, hazardous waste disposal, or for general inquiries concerning this program, contact EHS by emailing safety@towson.edu or by calling the Environmental Health & Safety (EHS) office at 410-704-2949.
2. Chemical Container Labeling
3. GHS Label Printing Instructions

Appendix A: Suggested Shelf Storage Pattern



A: Compatible Organic Bases

Diethylamine
Piperidine
Triethanolamine
Benzylamine
Benzyltrimethylammonium hydroxide

B: Compatible Pyrophoric & Water-Reactive Materials

Sodium borohydride
Benzoyl chloride
Zinc dust
Alkyl lithium solutions such as methyl lithium in tetrahydrofuran
Methanesulfonyl chloride
Lithium aluminum hydride

C: Compatible Inorganic Bases

Sodium hydroxide
Ammonium hydroxide
Lithium hydroxide
Cesium hydroxide

D: Compatible Organic Acids

Citric acid
Maleic acid
Propionic acid
Benzoic acid

E: Compatible Oxidizers Including Peroxides

Sodium hypochlorite
Hydrogen peroxide
3-Chloroperoxybenzoic acid

F: Compatible Inorganic Acids not Including Oxidizers or Combustibles

Hydrochloric acid

Phosphoric acid
Hydrogen fluoride solution

J: Poison Compressed Gases

Sulfur dioxide
Hexafluoropropylene

K: Compatible Explosives or Other Highly Unstable Materials

Picric acid dry(<10% H_2O)
Nitroguanidine
Tetrazole
Urea nitrate

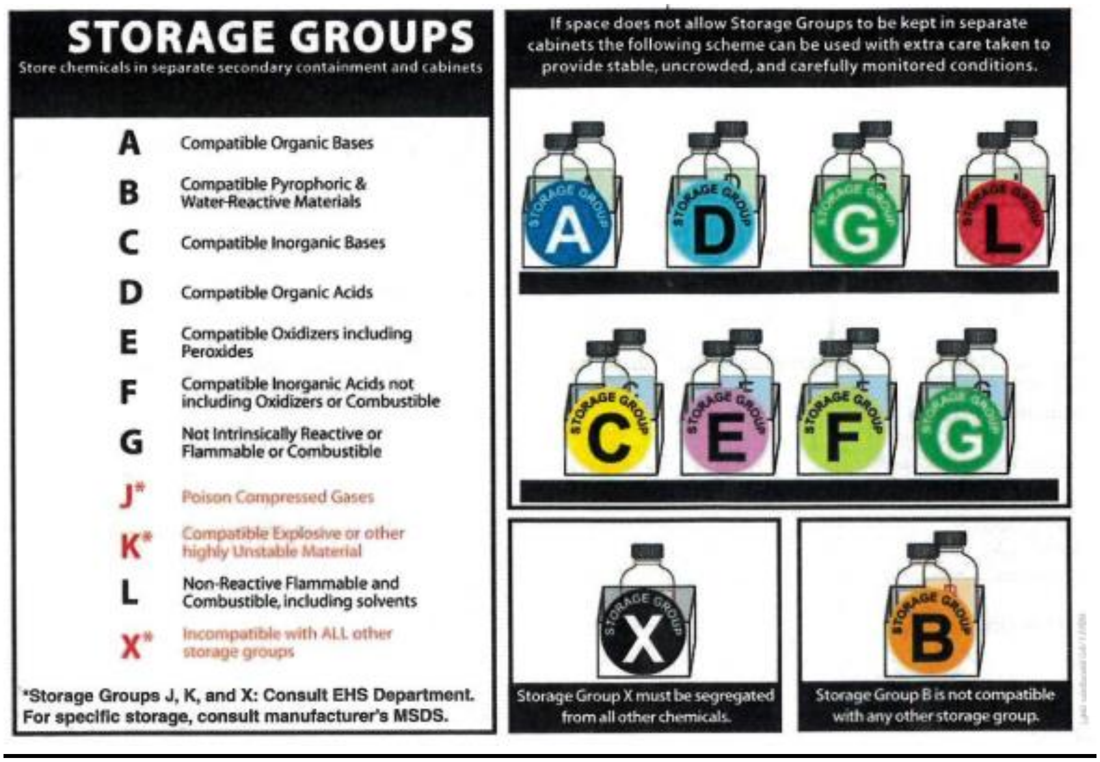
L: Nonreactive Flammables and Combustibles, Including Solvents

Benzene
Methanol
Toluene
Tetrahydrofuran

X: Incompatible with ALL Other Storage Groups

Picric acid moist (10-40% H_2O)
Phosphorus
Benzyl azide
Sodium hydrogen sulfide

Table 1. Compatible Storage Groups. The table displays groups of chemicals that are considered compatible.



STORAGE GROUPS

Store chemicals in separate secondary containment and cabinets

A	Compatible Organic Bases
B	Compatible Pyrophoric & Water-Reactive Materials
C	Compatible Inorganic Bases
D	Compatible Organic Acids
E	Compatible Oxidizers including Peroxides
F	Compatible Inorganic Acids not including Oxidizers or Combustible
G	Not Intrinsically Reactive or Flammable or Combustible
J*	Poison Compressed Gases
K*	Compatible Explosive or other highly Unstable Material
L	Non-Reactive Flammable and Combustible, including solvents
X*	Incompatible with ALL other storage groups

*Storage Groups J, K, and X: Consult EHS Department. For specific storage, consult manufacturer's MSDS.

If space does not allow Storage Groups to be kept in separate cabinets the following scheme can be used with extra care taken to provide stable, uncrowded, and carefully monitored conditions.

Storage Group X must be segregated from all other chemicals.

Storage Group B is not compatible with any other storage group.

Figure 1. Compatible Storage Groups & Patterns. The figure displays suggested arrangements for groups that correspond to chemicals in Table 1. This system should be used in conjunction with specific storage conditions, manufacturer's label, and relevant safety data sheets.

Appendix B: Storage of Flammable & Combustible Liquids

Flammable and combustible liquids are separated into the following classes according to NFPA:

Table 1 - Classification of Flammable and Combustible Liquids		
Class 1A Highly Flammable	Flash Point < 73˚F (22.8˚C) Boiling Point < 100˚F (37.8˚C)	Ex: Ethyl ether, Dimethyl sulfide, Petroleum ether
Class 1B Flammable	Flash Point < 73˚F (22.8˚C) Boiling Point ≥ 100˚F (37.8˚C)	Ex: Acetone, Toluene, Ethanol, Ethyl acetate, Hexane, Gasoline
Class 1C Flammable	Flash Point ≥ 73˚F (22.8˚C) Boiling Point < 100˚F (37.8˚C)	Ex: Amyl acetate, Butyric acid, Hexene, Xylene
Class II Combustible	Flash Point ≥ 100˚F (37.8˚C) & < 140˚F (60˚C)	Ex: Acetic acid, Cumene, Formaldehyde
Class IIIA Combustible	Flash Point ≥ 140˚F (60˚C) & < 200˚F (93.4˚C)	Ex: Benzaldehyde, Ethanolamine, Nitrobenzene

The NFPA has set limits for the storage of flammable liquids. Table 2 below provides the maximum container size for each class of flammable liquid.

Table 2 -
Maximum Container Sizes for Flammables & Combustibles

Container Type	**Flammable Liquid Class**			**Combustible Liquid Class**	
	1A	**1B**	**1C**	**II**	**IIIA**
Glass	1 Pt	1 Qt	1 Gal	1 Gal	5 Gal
Metal	1 Gal	5 Gal	5 Gal	5 Gal	5 Gal
Safety Can	2 Gal	5 Gal	5 Gal	5 Gal	5 Gal
Metal Drum (DOT)	60 Gal	60 Gal	60 Gal	60 Gal	60 Gal

The following are additional NFPA requirements for storage. For chemical stockrooms, individual evaluations will be necessary and, as a result, may not be bound to these requirements.

1. Not more than 10 gallons of Class I or Class II liquids combined shall be stored outside of a storage cabinet or storage room, except in safety cans.
2. Not more than 25 gallons of Class I or Class II liquids combined shall be stored in safety cans outside of a storage room or storage cabinet.
3. Not more than 60 gallons of Class IIIA liquids shall be stored outside of a storage room or storage cabinet.
4. Any quantity of liquids over this limit must be stored in an inside storage room or storage cabinet.
5. Approved storage cabinets shall not exceed 120 gallons of combustible and flammable liquids and not more than 60 gallons of the total may be flammable liquid. Not more than 3 storage cabinets will be within one fire area of a building.

A fire area, as defined by NFPA, is "an area of a building separated from the reminder of the building by construction having a fire resistance of at least one hour and having all communicating openings properly protected by an assembly having a fire resistance rating of at least one hour." Each laboratory should be considered an individual fire area.

Appendix C: Explosive & Reactive Laboratory Chemical Hazards

The variety of chemicals commonly present in a research laboratory poses the potential for accidental hazardous chemical reactions or explosions. A hazardous reaction occurs when two or more incompatible chemicals combine to result in an undesirable or uncontrolled reaction with adverse consequences. Such reactions may result when incompatible chemicals are accidentally spilled, when they are inadvertently mixed as chemical waste, or when they are unwittingly combined during experimental procedures. Hazardous reactions may cause any one or more of the following:

- Heat generation
- Fire
- Explosion
- Formation of toxic vapors
- Formation of flammable gases
- Volatilization of toxic or flammable substances
- Formation of substances of greater toxicity
- Formation of shock or friction sensitive compounds
- Pressurization in closed vessels
- Solubilization of toxic substances
- Dispersal of toxic dusts, mists, particles
- Violent polymerization.

It is easy to fall into the trap of becoming complacent with chemicals used every day in routine procedures. It is prudent to check for incompatibility wherever a change is made in chemical procedures. Incompatibility of chemicals is the prime reason for not storing chemicals on the shelf alphabetically. If there is an accident, the disaster is compounded by the adverse reaction. Safety Data Sheets will list "Reactivity Data" in one of the sections on the form. In addition, two good references of incompatible chemical combinations are: Handbook of Reactive Chemical Hazards; L. Bretherick, 6th Edition, 1999 (or most current edition); and Rapid Guide to Chemical Incompatibilities, R. Pohanish and S. Greene, 2nd Edition, 2003 (or most current edition).

Common Reactive Hazards in Laboratories

Listed below are specific chemical reactive hazards in laboratories that can lead to fires or explosions.

Acetylenic Compounds - are explosive in mixtures of 2.5-80% with air at pressures of two or more atmospheres, acetylene (C_2H_2) subjected to an electrical discharge or high temperature decomposes with explosive violence. Dry acetylides detonate on receiving the slightest shock.
Aluminum Chloride ($AlCl_3$) - should be considered a potentially dangerous material. If moisture is present, there may be sufficient decomposition [to give hydrogen chloride (HCl)] to build up considerable pressure. If a bottle is to be opened after long standing, it should be completely enclosed in a heavy towel.

Ammonia (NH_3) - reacts with iodine to give nitrogen triiodide, which is explosive, and with hypochlorites to give chlorine. Mixtures of NH_3 and organic halides sometimes react violently when heated under pressure.

Dry Benzoyl Peroxide ($(C_6H_5CO_2)_2$) - is easily ignited and sensitive to shock. It decomposes spontaneously at temperatures above 50°C. It is reported to be desensitized by addition of 20% water.

Carbon Disulfide (CS_2) - is both very toxic and very flammable; mixed with air, its vapors can be ignited by a steam bath or pipe, a hot plate, or a glowing light bulb.

Chlorine (Cl_2) - may react violently with hydrogen (H_2) or with hydrocarbons when exposed to sunlight.

Diazomethane (CH_2N_2) - and related compounds should be treated with extreme caution. They are very toxic, and the pure gases and liquids explode readily. Solutions in ether are safer from this standpoint. (See also "Organic Syntheses," Rabjohn, N., Ed.; Wiley: New York, 1963, Collective Volume IV, pp. 250 - 253).

Diethyl, Isopropyl, and other Ethers - (particularly the branched-chain type) may explode during heating or refluxing because of the presence of peroxides. Ferrous salts or sodium bisulfite can be used to decompose these peroxides, and passage over basic active alumina will remove most of the peroxidic material. Containers are to be marked with the date they are opened and discarded before they are out of date. For more detail, see Safe Handling of Peroxidable Compounds.

Dimethyl Sulfoxide [$(CH_3)_2SO$] - decomposes violently on contact with a wide variety of active halogen compounds. Explosions from contact with active metal hydrides have been reported. Its toxicity is still unknown, but it does penetrate and carry dissolved substances through the skin membrane.

Dry Ice - is not to be kept in a container that is not designed to withstand pressure. Containers of other substances stored over dry ice for extended periods generally absorb carbon dioxide (CO_2) unless they have been sealed with care. When such containers are removed from storage and allowed to come rapidly to room temperature, the CO_2 may develop sufficient pressure to burst the container with explosive violence. On removal of such containers from storage, the stopper should be loosened or the container itself should be wrapped in towels and kept behind a shield. Dry ice can produce serious burns (this is also true for all types of cooling baths). Do not store dry ice in walk-in cold rooms because it may result in oxygen-deficient atmosphere.

Drying Agents-Ascarite - is not to be mixed with phosphorus pentoxide (P_20_5) because the mixture may explode if it is warmed with a trace of water. Because the cobalt salts used as moisture indicators in some drying agents may be extracted by some organic solvents, the use of these drying agents should be restricted to gases.

Ethylene Oxide (C_2H_40) - has been known to explode when heated in a closed vessel. Experiments using ethylene oxide under pressure should be carried out behind suitable barricades.

Halogenated Compounds - Chloroform ($CHCL_3$), carbon tetrachloride (CCl_4), and other halogenated solvents should not be dried with sodium, potassium, or other active metal; violent explosions are usually the result of such attempts. Many halogenated compounds are toxic.

Hydrogen peroxide (H_20_2) - stronger than 3% can be dangerous; in contact with the skin, it may cause severe burns. Thirty percent H_20_2 may decompose violently if contaminated with iron, copper, chromium, other metals or their salts.

Liquid-Nitrogen Cooled Traps - when open to the atmosphere rapidly condense liquid air. When the coolant is removed, a pressure buildup may occur sufficient to shatter glass equipment. Only sealed or evacuated equipment should be cooled with liquid nitrogen.

Lithium Aluminum Hydride ($LiAlH_4$) - should not be used to dry methyl ethers or tetrahydrofuran; fires from this are very common. The products of its reaction with CO_2 have been reported to be explosive. Carbon dioxide or bicarbonate extinguishers are not to be used against $LiAlH_4$ fires, which should be smothered with sand or a metal-X extinguisher.

Oxygen Tanks - serious explosions have resulted from contact between oil and high-pressure oxygen. Oil should not be used on connections to an 0_2 cylinder or regulator.

Ozone (0_3) - is a highly reactive and toxic gas. It is formed by the action of ultraviolet light on oxygen (air) and, therefore, certain ultraviolet sources may require venting to the exhaust hood.

Palladium or Platinum on Carbon, Platinum Oxide, Raney Nickel, and other Catalysts - should be filtered from catalytic hydrogenation reaction mixtures carefully. The recovered catalyst is usually saturated with hydrogen and highly reactive and, thus, will ignite spontaneously on exposure to air. Particularly in large-scale reactions, the filter cake should not be allowed to become dry. The funnel containing the still-moist catalyst filter cake should be put into a water bath immediately after completion of the filtration.

Another hazard in working with such catalysts is the danger of explosion if additional catalyst is added to a flask in which hydrogen is present.

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

Perchlorates - the use of perchlorates should be avoided wherever possible. Perchlorates should not be used as drying agents if there is a possibility of contact with organic compounds or in proximity to a dehydrating acid strong enough to concentrate the perchloric acid ($HCl0_4$) to more than 70% strength (e.g., in a drying train that has a bubble counter containing sulfuric acid). Safer drying agents are to be used.

Seventy percent (70%) $HCl0_4$ can be boiled safely at approximately 200°C, but contact of the boiling undiluted acid or the hot vapor with organic matter, or even easily oxidized inorganic matter (such as compounds of trivalent antimony), will lead to serious explosions. Oxidizable substances must never be allowed to contact $HC10_4$. Beaker tongs, rather than rubber gloves should be used when handling fuming $HCl0_4$. Perchloric acid evaporations should be carried out in a hood that has a good draft. Frequent (weekly) washing out of the hood and ventilator ducts with water is necessary to avoid danger of spontaneous combustion or explosion if this acid is in common use.

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

Peroxides (inorganic) - when mixed with combustible materials, barium, sodium and potassium peroxides form explosives that ignite easily.

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

Phosphorus Trichloride (PCl_3) - reacts with water to form phosphorous acid, which decomposes on heating to form phosphine, which may ignite spontaneously or explode. Care should be taken in opening containers to PCl_3, and samples that have been exposed to moisture should not be heated without adequate shielding to protect the operator.

Potassium (K) - is in general more reactive than sodium; it ignites quickly on exposure to humid air and therefore, should be handled under the surface of a hydrocarbon solvent such as mineral oil or kerosene (see Sodium). Potassium may also form peroxides even while stored under oil.

Residues from Vacuum Distillations - (for example, ethyl palmitate) have been known to explode when the still was vented to the air before the residue was cool. Such explosions can be avoided by venting the still pot with nitrogen, by cooling it before venting, or by restoring the pressure slowly.

Sodium (Na) - should be stored in a closed container under kerosene, toluene or mineral oil. Scraps of Na or K are to be destroyed by reaction with n-butyl alcohol. Contact with water is to be avoided because Na reacts violently with water to form H_2 with evolution of sufficient heat to cause ignition. Use sand or metal-X extinguisher on alkali metal fires. Do not use CO_2.

Sulfuric Acid (H_2SO_4) - should be avoided, if possible, as a drying agent in desiccators. If it must be used, glass beads should be placed in it to help prevent splashing when the dessicator is moved. The use of H_2SO_4 in melting point baths should be avoided. (Silicone oil should be used). To dilute H_2SO_4, add the acid slowly to cold water.

Trichloroethylene (Cl_2CCHCl) - reacts under a variety of conditions with potassium or sodium hydroxide to form dichloroacetylene, which ignites spontaneously in air and detonates readily even at dry-ice temperatures. The compound itself is highly toxic and suitable precautions should be taken when it is used as a degreasing solvent. Methyl chloroform (1,1,1-trichloroethane) is a less toxic substitute.

Appendix D: Safe Handling of Peroxidizable Compounds

Peroxide formation in solvents and reagents has caused many accidents. Every worker must learn to recognize and safely handle peroxidizable compounds. Peroxides are formed by the reaction of a peroxidizable compound with molecular oxygen through a process called autoxidation or peroxidation. Peroxidizable compounds are insidious. Under normal storage conditions, they can form and accumulate peroxides, which may explode violently when subjected to thermal or mechanical shock.

Peroxides in solution at concentrations up to about 1 percent do not normally present thermal or shock hazards. Such solutions may be safely disposed of or treated to remove peroxides. However, should crystals form in a peroxidizable liquid or should discoloration occur in a peroxidizable solid, peroxidation may have already occurred. The product would then be considered extremely dangerous and should be disposed of without opening the container.
To prevent accidents caused by peroxidizable compounds, laboratory safety procedures should emphasize:

- Recognition of chemical structures that may form peroxides (See Appendix D, Table 1)
- Use of warning labels
- Controlled inventory of peroxidizable compounds
- Use of peroxide detection tests and peroxide removal procedures
- Proper safety equipment and process procedures

A. Peroxidizable Compounds

Some of the specific compounds that form peroxides during storage are included in Lists A, B, and C in Table 2. Those that form peroxides that may explode even without being concentrated are in List A. List B includes chemicals that are dangerous when concentrated by distillation or evaporation. Vinyl monomers that can form peroxides that may initiate explosive polymerization of the monomers are found in List C.

Peroxide accumulation is a balance between the rate of peroxide formation and the rate of peroxide degradation for the particular substance under the environment of the sample. For example, certain highly reactive compounds, such as organometallics, accumulate peroxide at low temperatures because the peroxide degradation rate is slowed relative to the formation rate. In contrast, less reactive compounds, such as hydrocarbons or ethers, are usually best kept at low temperatures.

The more volatile the peroxidizable compound, the easier it is to concentrate the peroxides. One should also remember that pure compounds are more subject to peroxide accumulation because impurities may inhibit peroxide formation or catalyze their slow decomposition.

B. Detection of Peroxides

Testing of ethers and other peroxide-forming solvents prior to distillation should be routine.

1. Peroxide Test Strips - Commercial test strips are available from Aldrich Chemical Company. These strips are convenient to use; however, they do not have the universality or the sensitivity of the ferrous thiocyanate test and their shelf-life is limited.
2. Ferrous Thiocyanate Test - Mix a fresh solution in the following proportions:
   - 5 mL of 1% ferrous ammonium sulfate
   - 0.5 mL of 0.5M sulfuric acid
   - 0.5 mL of 0.1M ammonium thiocyanate
   - Decolorize with a trace of zinc dust if necessary

   Shake an equal quantity of the solvent to be tested with the above reagent. The relation between color change and peroxide content is shown in Appendix D, Table 3.

C. Storage

Quantities of peroxidizable compounds should be purchased according to short-term needs. Only purchase quantities needed for immediate use; never stockpile. For instance, buy four (4) one-liter bottles of ether instead of one four-liter bottle. Purchase package sizes corresponding to use requirements to minimize exposure to air from multiple openings of the container. A tight cap on a nearly full bottle probably provides almost total protection against peroxide formation.

Peroxide accumulation can be held to very low levels by storage in reasonably full containers (25% maximum headspace) with TIGHT caps that are replaced promptly after use. Still more protection can be provided by flushing the headspace over peroxidizable compounds with nitrogen (inert gas) before closing the container. Vinyl monomers (Table 2, List C) containing certain inhibitors are exceptions and require air in the headspace.

The use of oxidation inhibitors is especially important in the safe handling of peroxidizable materials. Hydroquinone, alkyl phenols, aromatic amines, or similar materials are recommended by the manufacturers as being effective in preventing peroxide formation during storage of peroxidizable compounds. The inhibitor selected should be compatible with use or purity requirements of the compounds. A program of periodic testing and replenishing inhibitor levels should be followed during storage of peroxidizable materials.

Each laboratory should maintain a current on-hand inventory of peroxidizable compounds. This listing should be reviewed every semester and stored in a central location outside of the laboratory (or available online in CIDB) and immediately accessible to emergency responders. Those that are out of date should be immediately discarded through EHS.

List A (from Table 2) materials should be evaluated for peroxide content at least every three (3) months after opening and re-dated if safe, treated or discarded. Before disposal of any List A material, review the properties of the material to ensure safe disposal.

List B (Table 2) materials generally should not be stored longer than twelve (12) months after opening unless a suitable test shows they have not accumulated peroxide. If List B material gives a significantly positive test (red by the ferrous thiocyanate test), but must be retained, it must be treated to remove peroxide, repackaged, shown by test to be free of peroxide, and then re-dated on its label. (Di)ethyl ether must be removed after 12 months of storage, regardless of container status.

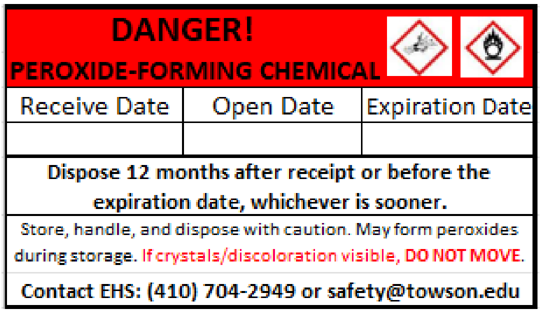
List C (Table 2) materials are vinyl monomers and should be stored for no longer than twelve (12) months unless test results show them to be free of peroxide. Commercial vinyl monomers usually contain additives (inhibitors), which inhibit peroxidation. Generally, storage of inhibited vinyl monomers should be under air rather than nitrogen or other inert atmosphere, because customary inhibitors are phenolic compounds, which require oxygen for their action. Most vinyl monomers may be polymerized without removal of inhibitor by proper adjustment of initiator concentration, thus making the isolation of the more hazardous uninhibited material unnecessary.

Uninhibited List C materials can be a significant hazard. Quantities of such uninhibited monomers greater than 500 g should be stored no longer than 24 hours. Small samples (less than 10 g may be stored longer than 24 hours with discretion. Generally, storage of uninhibited vinyl monomers should be under nitrogen and below room temperatures. For storage in excess of 24 hours, a suitable inhibitor should be added, and its name and quantity should be placed on the label.

In addition, each container of peroxide-forming chemicals <u>must</u> have the following dates written on the label.

- Date Received
- Date First Opened
- Date to be Discarded

EHS has pre-printed labels available. Contact EHS at (410) 704-2949 to request them.



DANGER!

PEROXIDE-FORMING CHEMICAL

Receive Date	Open Date	Expiration Date

Dispose 12 months after receipt or before the expiration date, whichever is sooner.

Store, handle, and dispose with caution. May form peroxides during storage. If crystals/discoloration visible, DO NOT MOVE.

Contact EHS: (410) 704-2949 or safety@towson.edu

Figure 1. Peroxide Former Label. The label displays a hazard statement, GHS pictograms, handling/storage information, and emergency contacts. The label also contains fields for user date inputs.

Peroxide-forming chemicals should be stored together in full, air-tight opaque containers at temperatures below 86°F (30°C) and in the dark. Use only refrigerators designated and UL-approved for flammable liquids or one that is explosion-proof as arcing contacts have been removed that might otherwise ignite vapors.

D. Removal of Peroxides

Peroxide impurities in water-insoluble solvents (e.g. diethyl ether, hydrocarbons) are easily purified by shaking with the following solution:

- 60 g of ferrous sulfate
- 6 mL of concentrated sulfuric acid
- 110 mL of distilled water

Water is introduced by this method, so post-drying will be required if a dry solvent is needed.

E. Disposal

Immediately set aside and **DO NOT USE** any peroxide-forming chemicals that have formed crystals, precipitate, solids, or an oily viscous layer, or any rusted, damaged, undated or suspicious containers of peroxide-forming chemicals. If you discover, or suspect you have discovered, any old, potentially explosive or reactive chemical, **do not handle them.** Contact EHS immediately at either (410) 704-2949 or at safety@towson.edu. Please include the name of the chemical(s), the quantity (1 x 1-pint, etc.) and its location (SC 0123, under the hood, etc.).

Never attempt to force open a rusted or jammed cap or a cap encrusted with scale on a container of peroxide-forming chemicals. Never attempt to clean by scraping or rubbing glassware or other containers if an oily deposit or crusty residue is present.
Empty containers of ethers and other peroxide-formers are to be flushed with water before discarding. Empty containers are not regulated for disposal as hazardous wastes and may be disposed via traditional domestic waste channels.

F. Distillation and Evaporation Precautions

Testing peroxidizable solvents for peroxides prior to distillation or evaporation should be routine. One common error is distilling too close to dryness; leave at least 10% bottom to ensure complete safety.

G. Safety Audit

A safety audit should be performed before starting any chemical experiment in the laboratory. This would include a review of possible hazards from the use of peroxidizable chemicals in the experiment. Peroxidation may have already occurred in one or more of the starting materials; it may occur during the process, or in the storage of the products. In every chemical process, the following factors should be considered relative to (a) the starting materials, (b) the process itself, and (c) the products:

- Structure - are peroxidizable structures present or being formed?

- Process conditions - will the process condition favor initiation of peroxidation and accumulation of peroxides?
- Storage - will storage containers and conditioners reduce peroxide initiation and accumulation, and are all products properly inhibited and labeled?

If the audit indicates that peroxidation or peroxides are present, the described procedures of handling, testing, and removal should be followed.

As noted previously, peroxidation in a chemical process may not only be a serious hazard because of the explosion potential, but it also may affect the results of an experiment because of lower yield and unwanted impurities.

Table 1. Peroxide-Forming Structures. The table lists peroxide-forming organic structures in approximate order of decreasing hazard, with the most hazardous structure listed first.

Structure	Example
1. Ethers with alpha hydrogen atoms	Isopropyl ether, ethyl ether, glyme
2. Acetals with alpha hydrogen atoms	Acetal, benzylacetal
3. Olefins with allylic hydrogen atoms	Butylene, cyclohexene
4. Chloroolefins and fluoroolefin	Tetrafluoroethylene
5. Vinyl halides, esters, and ethers	Vinyldene chloride, vinyl chloride, vinyl acetate
6. Dienes	Butadiene, chloroprene
7. Vinylacetylenes with alpha hydrogen atoms	Diacetylene, vinylacetylene
8. Alkylacetylenes with alpha hydrogen atoms	3-Methyl-1-butyne
9. Alkylarenes that contain tertiary hydrogen atoms	Isopropyl benzene
10. Alkanes and cycloalkanes that contain tertiary hydrogen atoms	Ethylcyclohexane
11. Acrylates and methacrylates	Methylmethacrylate, acrylonitrile
12. Secondary alcohols	Sec-butyl alcohol, diphenylmethanol
13. Aldehydes	Benzaldehyde
14. Ketones with alpha hydrogen atoms	Diisopropyl ketone, methyl ethyl ketone (MEK)
15. Ureas, uramides, lactams with hydrogen atom on carbon atom attached to nitrogen	N-Ethylacetamide, N-isopropylacetamide

Table 2. Common Compounds That Form Peroxides During Storage. Reactive compounds are listed by expiration and hazard type.

List A, Red Label (3 months) Peroxide Hazard on Storage	List B, Yellow Label (12 months) Peroxide Hazard on Concentration	List C, Yellow Label (12 months) Hazard Due to Peroxide Initiation of Polymerization
Isopropyl ether	(Di)ethyl ether	Butadiene
Divinyl acetylene	Tetrahydrofuran	Tetrafluoroethylene
Vinylidene chloride	Dioxane	Chlorotrifluoroethylene
Potassium metal	Acetal	Styrene
Sodium amide	Methyl isobutyl ketone	Vinyl acetylene
	Ethylene glycol dimethyl ether (Diglyme)	Vinyl acetate
	Glyme	Vinyl chloride
	Vinyl ethers	Vinyl pyridine
	Dicyclopentadiene	Chlorobutadiene (chloroprene)
	Diacetylene	9,10-Dihydroanthracene
	Methyl acetylene	Idene
	Cumene	Dibenzocyclopentadiene
	Tetrahydronapthalene	
	Cyclohexene	
	Methylcyclopentane	
	Tert-Butyl alcohol	

***** When stored as a liquid, the peroxide-forming potential increases and certain of these monomers (especially butadiene, chloroprene, and tetrafluoroethylene) should then be considered as List A compounds.

Table 3. The Ferrous Thiocyanate Test. The table displays the relation between color change and peroxide content of a compound in % peroxide (as H_2O_2).

Color	% Peroxide (as H_2O_2)
Pink, barely discernible	**0.001**
Pink to Cherry Red	**0.002**
Red	**0.008****
Deep Red	**0.04****

**A percentage of 0.008 or more is a hazard

Appendix E: Potential Carcinogens

For storage purposes, the following is a list of substances NIOSH considers to be potential occupational carcinogens. A number of the carcinogen classifications deal with groups of substances: aniline and homologs, chromates, dinitrotoluenes, arsenic and inorganic arsenic compounds, beryllium and beryllium compounds, cadmium compounds, nickel compounds, and crystalline forms of silica. There are also substances of variable or unclear chemical makeup that are considered carcinogens, coal tar pitch volatiles, coke oven emissions, diesel exhaust and environmental tobacco smoke.

Some of the potential carcinogens listed in this index may be re-evaluated by NIOSH as new data become available and the NIOSH recommendations on these carcinogens either as to their status as a potential occupational carcinogen or as to the appropriate recommended exposure limit may change. The listings are placed in alphabetical order for convenience only, not based on the level of severity.

A			
Acetaldehyde	Aldrin	*o*-Anisidine	Asbestos
2-Acetylaminofluorene	4-Aminodiphenyl	*p*-Anisidine	Asphalt fumes
Acrylamide	Amitrole	Arsenic and inorganic arsenic compounds	
Acrylonitrile	Aniline and homologs	Arsine	

B			
Benzene	Benzidine-based dyes	Butadiene	
Benzidine	Beryllium	*tert*-Butyl chromate; class, chromium hexavalent	

C			
Cadmium dust and fume	Chlordane	Chloromethyl methyl ether	Chrysene
Captafol	Chlorinated camphene	bis(Chloromethyl) ether	Coal tar pitch volatiles; class, coal tar products
Captan	Chlorodiphenyl (42% chlorine); class polychlorinated biphenyls	*B*-Chloroprene	Coke oven emissions
Carbon black (exceeding 0.1% PAHs)	Chlorodiphenyl (54% chlorine); class polychlorinated biphenyls	Chromium, hexavalent [Cr(VI)]	
Carbon tetrachloride	Chloroform	Chromyl chloride; class, chromium hexavalent	

D			
DDT (dichlorodiphenyltrichloroethane)	Dichloroacetylene	Dieldrin	1,1-Dimethyl hydrazine; class, hydrazines
Di-2-ethylhexyl phthalate (DEHP)	*p*-Dichlorobenzene	Diesel exhaust	Dimethyl sulfate
2,4-Diaminoanisoleo	3,3'-Dichlorobenzidine	Diglycidyl ether (DGE); class, glycidyl ethers	Dinitrotoluene
o-Dianisidine-based dyes	Dichloroethyl ether	4-Dimethylaminoazobenzene	Dioxane
1,2-Dibromo-3-chloropropane (DBCP)	1,3-Dichloropropene	Dimethyl carbamoyl chloride	

E-G			
Environmental tobacco smoke	Ethylene dibromide	Ethyleneimine	Gallium arsenide
Epichlorohydrin	Ethylene dichloride	Ethylene thiourea	Gasoline
Ethyl acrylate	Ethylene oxide	Formaldehyde	

H-K		
Heptachlor	Hexachloroethane	Hydrazine
Hexachlorobutadiene	Hexamethyl phosphoric triamide (HMPA)	Kepone

M			
Malonaldehyde	Methyl chloride	Methyl hydrazine; class, hydrazines	4,4-Methylenedianiline (MDA)
Methoxychlor	Methylhydrazine	4,4'-Methylenebis(2-chloroaniline) (MBOCA)	
Methyl bromide; class, monohalomethanes	Methyl iodide; class, monohalomethanes	Methylene chloride	

N			
a-Naphthylamine	Nickel carbonyl	*p*-Nitrochlorobenzene	*N*-Nitrosodimethylamine
b-Naphthylamine	Nickel sulfide roasting	2-Nitronaphthalene	
Nickel, metal, soluble, insoluble, and inorganic; class, nickel, inorganic	4-Nitrobiphenyl	2-Nitropropane	

P			
Pentachloroethane; class, chloroethanes	Phenylhydrazine; class, hydrazines	Propylene dichloride	
N-Phenyl-*b*-naphthylamine; class, *b*-naphthalene	Propane sultone	Proplyene imine	
Phenyl glycidyl ether; class, glycidyl ethers	*b*-Propiolactone	Propylene oxide	

R-S			
Radon	Silica, crystalline cristobalite/quartz/tripoli and tridymite	Soapstone, total dust silicates	
Rosin core solder, pyrolysis products (containing formaldehyde)	Silica, fused		

T			
Tremolite silicates	Titanium dioxide	*o*-Toluidine-based dyes	1,2,3-Trichloropropane
2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (TCDD) (dioxin)	Toluene diamine (TDA)	*p*-Toluidine	
1,1,2,2-Tetrachloroethane	Toluene diisocyanate (TDI)	1,1,2-Trichloroethane; class, chloroethanes	
Tetrachloroethylene	*o*-Toluidine	Trichloroethylene	

U-Z			
Uranium, insoluble compounds	Vinyl chloride	Welding fumes, total particulates	
Uranium, soluble compounds	Vinyl cyclohexene dioxide	Wood dust	
Vinyl bromide; class, vinyl halides	Vinylidene chloride (1,1-dichloroethylene); class, vinyl halides)	Zinc chromate; class, chromium hexavalent	

Appendix F: Chemical Storage Regulations & Standards

29 CFR 1910.1200: Hazard Communication
https://www.osha.gov/laws-regs/regulations/standardnumber/1910/1910.1200

29 CFR 1910.1450: Occupational Exposure to Hazardous Chemicals in Laboratories
https://www.osha.gov/laws-regs/regulations/standardnumber/1910/1910.1450
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