Chapter 5 Managing Hazardous Materials at C.O.S.E.

5.1 Procuring Materials for Laboratories

It is important to know what you already have before ordering hazardous materials for the coming semester or school year. Keep your list (or inventory) of hazardous materials up-to-date and use the information for training, planning, and ordering. Order only what you think you can use up during the year to minimize storage needs.

- Before receiving a hazardous substance, make sure you have the MSDS and know how to safely store and handle it.
- Reject any container without a label specifying the contents and significant hazards.
- Notify the stockroom of new acquisitions so they can be added to the inventory.
- Avoid purchasing chemicals in bulk because of the strain on limited space, the expense of ultimate disposal of unused quantities, and the potential hazards caused by large quantities in a small space.

What is the policy for donated chemicals?

The University does not accept donated chemicals without prior approval from the University EHOS Dept.

[Very often the chemicals are near their expiration date or are in quantities that you won't be able to use up. The problem: Although this does save the donating company the expense of disposing of these chemicals, the University ends up paying for the disposal. Disposal costs are expensive and the University spends much more than the initial cost savings. The University is then the new generator of the waste and is responsible for it forever. The EPA (Environmental Protection Agency) uses the phrase, "from the cradle to the grave".]

What are recommended distribution practices?

- Distribute chemicals in the smallest quantities possible.
- If you must take a chemical to the stockroom or even down the hall, try using a bottle carrier, bucket or other carrying device. Use the freight elevator when possible. *It is not good practice to carry unprotected hazardous liquids in a dirty lab coat and gloves in a passenger elevator with the public.*
- Avoid buying liquids in bulk whenever possible. *Unless large quantities are used regularly, bulk liquids often end up wasting storage space and costing more in disposal than any savings in the initial purchase.*
- When transferring flammable liquids from drums 5 gallons or greater into small containers, ground the drum and bond the small container to the drum. *This practice can prevent static build-up and the associated electrical shock hazard.*

What are some good inventory management practices for stockrooms and labs?

To prevent unwanted chemical reactions, you must establish a chemical storage system in your lab that separates incompatibles by distance or containment. You must also plan experiments to minimize the risk of unwanted reactions.

- Clean up minor spills promptly and thoroughly to prevent accidental contamination of clothing or other chemicals.

- Use secondary containers to store chemicals on counters, fume hoods and to separate incompatibles.
- When transferring a chemical to a different container, affix an identification label onto the transfer container. Make sure the label is secure and legible.
- Mark the date received for all incoming chemicals– including those from vendors.
- Segregate chemicals by hazard class prior to restocking them
- Store flammables in a storage cabinet for flammable liquids or safety cans – avoid storing on the floor.
- Discard chemicals manufactured in-house within one year, unless part of current research
- Periodically evaluate stored chemicals and discard those that are past their shelf life
- Store chemicals reactive to air, water, light, and room temperature clustered together. Improperly stored chemicals like this degrade quickly so check them frequently.
- Avoid storing chemicals in beakers or test tubes topped with paraffin or foil.

5.2 Storing and Using Lab Chemicals

What are some guidelines for safely using compressed gas cylinders?

Compresses gas cylinders can be very hazardous if mishandled. Common hazards include mixing of incompatible gases, asphyxiation in confined areas, explosion from leaking flammable or oxidizing gas, and sudden release of pressure from a broken valve.

- Contact the department stockroom for assistance with gas cylinders.
- Always secure cylinders to a wall or heavy furnishings.
- Keep caps screwed on unless actively using the cylinder.
- Transport cylinders with caps screwed on using a cart designed for moving cylinders.
- Don't lift a cylinder by its cap.
- Store flammable gases separately (by at least 20 ft. or with a fire wall) from oxygen and open flames.
- Separate incoming cylinders from empty ones and mark them with tags as "empty" "full", or "in service" as appropriate.
- Store gas cylinders that won't be used during the summer or regular semester. ***Remove the regulator and replace it with a securely screwed on storage cap.***
- Install in-line filters or devices to prevent flashbacks or spread of bacteria and other biohazards when using compressed gases

How should highly reactive chemicals be handled?

Highly reactive chemicals such as organic peroxides and perchloric acid must be labeled "DANGER! Highly Reactive Material". Use only the smallest amounts possible to minimize risks. If a refrigerator or inert atmosphere is necessary to keep these materials stable, note this clearly on the container label. You should also install a warning system and/ or back up system in case of system failure.

- Write date received on the label
- Store highly reactive chemicals as indicated on the manufacturer's label.
- Purge these chemicals from inventory every year.

What storage practices does the reference "Prudent Practices in the Laboratory" recommend?

Prudent Practices in the Laboratory has an entire chapter devoted to managing chemicals, namely Chapter 4, "Management of Chemicals". This is an excellent reference for what your peers are (or should be) doing. To see a review copy, contact the COSE Health & Safety Specialist at x8-6892.

Some of the more common practices are listed below for you to consider when arranging your laboratory for optimum performance.

- Separate chemicals by hazard class first before arranging them alphabetically.
- Avoid storing chemicals on bench tops, fume hoods or on the floor and keep them away from sunlight and hot conditions. Follow manufacturer's storage recommendations to ensure a stable product.
- Inspect storage containers periodically for damage, integrity or evidence of unwanted reactions. Clean spillage on the outside to prevent inadvertent contact by other lab occupants.
- Store chemicals below eye level on shelves with doors, lips or other restraints.
- Place the user's name and the date received on all purchased materials.
- Keep volatile toxics and smelly chemicals in a ventilated cabinet or fume hood when handling them.
- Use corrosion resistant storage trays or secondary containment to retain materials if the primary container breaks or leaks. These can be used to separate incompatibles if space is tight.

Which hazard classes are considered incompatible?

In most cases, the materials below should be stored separately.

Flammable Liquids	Oxidizers	Biohazards
Organic Acids	Hydrides	Radioactives
Mineral Acids	Halogenated Solvents	Flammable Solids

Separate chemicals into their organic and inorganic families and then related and compatible groups as shown below. In many cases, separation of chemical groups can be maintained by using different shelves within the same cabinet or by storing in separate secondary containers.

Table 7: Incompatible Chemicals from "Prudent Practices in the Laboratory".

Organic Family	**Inorganic Family**
Metals, hydrides	Acids, peracids, anhydrides
Halides, sulfates, sulfites, thiosulfates, phosphates, halogens	Alcohols, glycols, amines, amides, imines, imides
Amides, nitrites, azides, nitrates *(except ammonium nitrate)*	Hydrocarbons, esters, aldehydes
Hydroxides, oxides, silicates, carbonates	Ethers, ketones, ketenes, halogenated hydro carbons, ethylene oxide
Arsenates, cyanides, cyanates	Isocyanates, epoxy compounds

Table 7: Incompatible Chemicals from "Prudent Practices in the Laboratory".

Borates, chromates, manganates, permanganates	Peroxides, hydroperoxides, azides
Nitric acid, inorganic acids	Phenols, cresols
Sulfur, phosphorous, arsenic, phosporous pentoxide	
Sulfides, selenides, phosphides carbides, nitrides	

What are some guidelines for storing incompatible materials?

- Store inorganic acids in a (preferably non-metal or lined) cabinet in a plastic secondary storage tray. Strong organic acids may be stored in the same cabinet only if they are in a separate storage tray or other secondary containment.
- Store strong bases in a (preferably non-metal or lined) cabinet in a plastic secondary storage tray. Acids may be stored in the same cabinet only if they are in a separate storage tray or other secondary containment.
- Keep flammable solids and other water reactive chemicals in a dry location away from organic solvents.
- Keep strong oxidizers away from acids and organic solvents.
- Always store nitric acid, a strong oxidizer, away from acetic acid, bases and organics.
- Store acetic acid with other organic acids because it is corrosive as well as combustible. However, it is acceptable to store acetic acid with flammable solvents as long as it is separated with secondary containment. Keep away from strong nitric acid!
- Store perchloric acid and strong (70%) nitric acid in separate trays made of resistant plastic or glass, as they are both highly corrosive and reactive to many materials.
- Do not store halogenated solvents, such as methylene chloride, in flammable storage cabinets because they are not flammable and may pose a hazard to fire fighters if they mix and catch fire. *Phosgene (a toxic gas) is formed as a by-product of combustion.*
- Separate pyrophoric chemical compounds from other flammable liquids.

What are some chemical-specific storage policies?

- Hydrides: Store separately in labeled metal containers.
- Flammable solids: Store separately in labeled metal containers.
- Pyrophorics: Store in refrigerators designated as "explosion-proof".
- Cans: Bottles shipped in sealed cans must be opened upon receipt and inspected. Don't store such cans unopened in the laboratory.
- Ether: Date containers upon receipt and check expiration dates. Ether must be used within 1 year or before the expiration date, whichever is less.
  The practice of buying drums of ether has been discontinued.
- Halogenated solvents: Unless the label says it's flammable, store separately from flammable liquids. Any cabinet or refrigerator marked "Flammable" must not have any non-flammable halogenated solvents inside.
- Carcinogens: Human carcinogens must have a have a prominent "Carcinogen" label attached to each container. Limit access to authorized individuals only.
- Store organic peroxides at the lowest possible temperature, consistent with the solubility and freezing temperature of the material.

What is the policy for using refrigerators and freezers for storing hazardous materials?

Each refrigerator and freezer used in the COSE must have a label either designating it for **"Food Only"** or prohibiting food, i.e., **"No Storage of Food or Beverages"**.

Refrigerators not designed to hold flammable or explosive materials, should not have such materials stored inside. For chemicals requiring refrigeration, use refrigerators designed and labeled for storing flammables. In the Chemistry & Biochemistry department, refrigerators are available for the following hazard classes:

- Flammables
- Non-flammables
- Non-flammable halogenated materials
- Pyrophorics

5.3 Highly Toxic Materials

Sloppy handling can result in unwanted exposures. Some chemicals, like methyl mercury, aniline, and hydrogen fluoride absorb readily through the skin and are deadly. Others, like ethidium bromide are strong mutagens but the user may experience no obvious ill effects. Chronic exposure to carcinogenic chemicals can also cause illness in the long term but without obvious short term ill effects.

Check the list of selected highly toxic chemicals in ***Appendix E*** to help you decide whether special precautions and pre-approvals make sense in your operation. Note that you must be able to justify your reasoning if asked.

How should highly toxic materials be handled?

- Designate an area for handling dangerous substances in the laboratory:

DANGER

"Specific Agent"

AUTHORIZED PERSONNEL ONLY

See "Faculty Name" for more information.

- Institute a prior approval system to protect students from inadvertent handling of dangerous substances. See ***Appendix D*** for the "Prior Approval" form.
- Minimize quantities of these chemicals and keep the lowest possible concentrations when in solution.
- Conduct all work with genotoxins, reproductive toxins, carcinogens, and acutely toxic materials within a certified functioning fume hood, biological safety cabinet, ventilated glove box, sealed system or other system designed to control exposure.
- Do not exceed OSHA permissible exposure limits (PEL's) for chemicals in your work area. Usually expressed as an eight-hour time weighted average concentration, a PEL is the maximum concentration of a specific chemical in inhaled air that the average healthy worker may be exposed to each day for a lifetime of work without significant adverse health effects.

Table 8: Special Practices for Dangerous Substances

Type of Substance	Good Practice or Procedure
Fine powders	Keep in closed containers. Use only in areas with minimal air currents.
Hydrogen fluoride	Must be used in presence of calcium gluconate. After any skin contact, pour calcium gluconate on the affected area immediately to neutralize the reaction. Hydrogen fluoride absorbs through skin and targets the cal cium in bones with serious and potential deadly effects.
Aniline	Skin contact can cause internal oxygen deficiency and a bright blue tinge to the exposed person's skin. Call 911 immediately.
Carcinogens *(such as benzene and acrylamide)*	Benzene and acrylamide are potent human carcinogens. Avoid skin contact and inhalation of vapors. Report possible exposures to the EHOS Dept. at x8-1449.

5.4 Minimizing Chemical Storage

When should I consider discarding chemicals?

Take into account a chemical's replacement cost, availability, hazard, and storage requirements when deciding whether to keep it or discard it. Buy only what you need and can use in a reasonable amount of time.

- Aggressively purge smelly chemicals from storage before they become offensive.
- Discard containers that may be compromised. Look for evidence like excessive rust, bulges, or pooled material underneath. Be sure to evaluate the safety of handling such containers before moving them.
- Check the expiration date and discard old and expired chemicals.
  [While it is true that suppliers may choose a date for marketing reasons, rather than because the substance is not longer usable, if it is more than a couple of years beyond that date, it should be discarded. Make room for storing chemicals you do need and will use.]
- Dispose of materials which do not have an identified use within a *reasonable* period, such as 3 years. Stable, relatively non-hazardous substances may be kept longer, as long as they still have a legitimate use.
  [Replace deteriorating labels if the container itself is still in good condition. Do this before the information is obscured or lost. If the contents cannot be identified by a knowledgeable person, then it must be disposed of a unknown hazardous waste.]
- Establish a policy to address faculty retirement and discard or archive materials.
- Remove graduate student research products once he or she graduates, if materials are no longer needed. If the materials are necessary for further research, follow the archival policy. Establish a clean-out policy for your laboratory to avoid accumulating orphaned chemicals.

- If the chemical looks like it has undergone a physical change, such as crystals have formed, or it has dried out, discard it regardless of the expiration date.
  Some chemicals, such as picric acid, Bouin's Reagent, and trinitrobenzene can be dangerous if allowed to dry out. Clear out old ether and tetrahydrofuran containers.
- Justify the use of highly toxic or carcinogenic chemicals in your program. Whenever possible, substitute less toxic chemicals for extremely toxic chemicals like aniline and class A carcinogens like benzene.

Why should I discard chemicals I may use one day (maybe)?

If the chemical is very old, you would probably rather use something that you are sure is still pure for any important research.

As of 1980, laws requiring chemical name and hazard information on all containers went into effect. If the label on your original bottle does not have physical and health hazards clearly printed on it, then it is more than 20 years old and you should get rid of it!

- If there is evidence of deterioration or physical change, it may no longer be a useful reagent and should be designated as waste;
- You free up valuable work and shelf space;
- Annual inventories are much quicker and more accurate when the quantity is manageable and storage is well organized.
- You decrease the chance for tripping over a chemical or accidentally knocking if off the shelf due to the clutter and crowded work space;
- Ongoing culling of inventory saves the University money because the practice minimizes the following expensive services:
  - large laboratory clean-outs when a researcher moves
  - extensive analysis for disposal of unknowns
  - fines from regulatory agencies for poor storage practices.

How should archival chemicals be stored?

Sometime prior to a student's graduation or completion of a research project, all chemicals created by the student should either be archived for future use or disposed appropriately. In addition, student laboratory notebooks should be collected and stored either in the PI's laboratory or office. When faculty retire, use this same practice to handle their chemicals to avoid unnecessary storage of unwanted reagents and creation of "unknowns".

Chemicals that must be saved for some legitimate purpose need to be securely closed and labeled describing this purpose. In addition to the purpose of the chemical sample, the following information must be included on a label or tag securely attached to the container:

- Researcher name
- Identification of the material including laboratory notebook reference
- List of components known to be hazardous along with their hazards
- Date created

5.5 Managing Hazardous Waste

Waste can be defined as substances that are expired, outdated, contaminated or otherwise no longer useful. A "hazardous" waste is a substance that can cause harm to people or to the environment. The person the substance belongs to who decides that it is now waste material is the "generator" of the waste.

Typically the Principal Investigator or lab manager is the generator of the waste and so is responsible for handling the waste appropriately in compliance with campus policy and hazardous materials permit. An identification tag must be affixed to each container as soon as the first drop of waste material goes in. An example of a correctly filled-out tag is included in **Appendix D**.

How should a waste collection area be set-up?

A waste collection area, known as "Satellite Accumulation Area" (SAA), must be an area separated from non-waste chemicals. In tight spaces, secondary containment can be used to separate waste from non-waste and incompatibles from each other.

- Choose a hazardous waste collection area in or near the laboratory or shop.
- Post a sign designating this area as the "Satellite Accumulation Area" (SAA) for your hazardous waste.
- Inform your lab assistants that an SAA is a discrete portion of the laboratory just for waste storage. Government inspectors look at these areas very closely to make sure they are in compliance with EPA regulations covering hazardous waste.
- Separate wastes according to chemical compatibility and waste type. *Biohazardous waste, radioactive waste, broken glass, solid waste, and chemical hazardous waste must be stored in separate secondary containers or areas.*
- Do not mix wastes unless you know they are compatible (Many organic solvent wastes are compatible).
- Do not mix halogenated waste with non-halogenated wastes, even if they are chemically compatible, because mixing them adds significantly to disposal costs.

What are the requirements for maintaining a compliant waste collection area?

The generator of the waste is responsible for identifying the waste, completing the waste ID tag, and for making sure waste is stored properly at all times. The generator may delegate this task to someone else, but the generator is still ultimately responsible.

> **Stockroom staff is NOT responsible for identifying wastes or filling out waste ID tags for others.**

Review the following information with everyone working in your lab or workshop to make sure everyone knows how to handle hazardous waste generated in the lab.

- Warn lab workers not to pour hazardous waste into the sink or floor drains.
- Make it clear who is responsible for obtaining, labeling and tagging waste bottles.
- Show where to get containers to collect waste (usually from the stockroom).
- Demonstrate how to fill out the waste identification tag.

Follow this procedure once waste has been generated:

- Affix a COMPLETED hazardous waste ID tag to the bottle
- Separate wastes according to chemical compatibility and waste type.
- Keep waste containers closed when not directly adding waste. When finished adding waste, do not leave funnels in containers. Replace the cap.
- Wipe off spilled materials on the outside of containers to minimize inadvertent exposure to the material.
- Take waste to the stockroom for collection when the container is full OR it is nearing 60 days from the date written on the tag. (This date is the day the first drop of waste was added.)

Important Note:

Lab costs for identifying unknowns can run into thousands of dollars!

How can a waste be declared non-hazardous?

Justify and document the reasoning for declaring a lab waste as "non-hazardous". The term "hazardous waste" has legal implications requiring knowledgeable disposal practices. EPA, Cal-EPA, county health, water treatment district and the fire department all regulate waste to some extent. As the generator of the waste, you must be able to justify your collection and disposal protocols.

If you think a waste stream you generate isn't hazardous, obtain a "Petition for Non-Hazardous Waste Status" from the COSE Health & Safety Specialist. You'll have to describe your process for generating the waste and note the concentration of each material in your wastestream. Upon receipt, University EHOS will evaluate your request and let you know if it is okay to change your disposal practice.

To see a copy of the **"Petition for Non-Hazardous Waste Status,"** see ***Appendix D***.

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