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The George Washington University Hazardous Materials Management Plan

Introduction

The George Washington University is committed to providing a safe laboratory environment for its faculty, staff, students and visitors. The goal of the Hazardous Materials Management Plan (HMMP) is to minimize the risk of injury or illness to laboratory workers by ensuring that they have the training, information, support and equipment needed to work safely in the laboratory.

The HMMP is comprised of two main elements. The first part describes potential hazards of hazardous materials found in a laboratory and reviews safe laboratory practices. The second part describes the hazardous materials stored in laboratories at GW, including intended storage and use areas and chemical inventory.

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Part I: Laboratory Hazards and Safe Laboratory Practices

1.1 Chemical and Hazard Identification

Chemical manufacturers are required to perform an assessment of the physical and health hazards of the chemicals they produce. This information must be made available in two places: the chemical label and the material safety data sheet (MSDS). Thus, the information found on the original container label and the MSDS may provide a great deal of information about the identity of the chemical constituents and their health and physical hazards.

1.1.1 Labels

The manufacturer's label should be kept intact. Do not intentionally deface or obscure the label or the hazard warnings. When a chemical is transferred from the original container into a secondary container for storage, the new container should be labeled with the name of the product, the chemical constituents and the primary hazard warnings.

1.1.2 Material Safety Data Sheets

All chemical manufacturers or distributors are required to conduct a hazard evaluation of their products and include the information on a material safety data sheet (MSDS). The manufacturer or distributor is required to provide an MSDS with the initial shipment of their products. Any MSDSs received by the laboratory must be maintained in a central location that is readily accessible at all times in the laboratory or the department.

If an MSDS is not on hand, check the Risk Management web page, <http://www.gwu.edu/%7Eriskmgnt/msds.cfm>, for connections to on-line sources of MSDSs. If the MSDS cannot be found, contact the manufacturer or distributor at the number listed on the container label and request an MSDS. If the manufacturer does not provide one within a few days, contact Risk Management for assistance.

1.2 Laboratory Basics

Every laboratory worker should observe the following rules:

- Know the potential hazards and appropriate safety precautions before beginning work. Ask and be able to answer the following questions:
 - What are the hazards?
 - What are the worst things that could happen?
 - What do I need to do to be prepared?
 - What work practices, facilities or personal protective equipment are needed to minimize the risk?
- Know the location and how to use emergency equipment, including safety showers and eyewash stations.
- Familiarize yourself with the emergency response procedures, facility alarms and building evacuation routes.
- Know the types of personal protective equipment available and how to use them for each procedure.

- Be alert to unsafe conditions and actions and bring them to the attention of your supervisor or lab manager immediately so that corrections can be made as soon as possible.
- Prevent pollution by following waste disposal procedures. Chemical reactions may require traps or scrubbing devices to prevent the release of toxic substances to the laboratory or to the environment.
- Position and clamp reaction apparatus thoughtfully in order to permit manipulation without the need to move the apparatus until the entire reaction is completed. Combine reagents in the appropriate order and avoid adding solids to hot liquids.

1.3 Chemical Storage

Many local, state and federal regulations have specific requirements that affect the handling and storage of chemicals in laboratories.

1.3.1 General Considerations

- In general, store materials and equipment in cabinets and on shelving provided for such storage.
- Avoid storing materials and equipment on top of cabinets. If you must place things there, however, you must maintain a clearance of at least 18 inches from the sprinkler heads or (if no sprinkler heads are present) 24 inches from the ceiling.
- Be sure that the weight of the chemicals does not exceed the load capacity of the shelf or cabinet.
- Wall-mounted shelving must have heavy-duty brackets and standards. This type of shelving is not recommended for chemical storage.
- Cabinets for chemical storage must be of solid, sturdy construction, preferably hardwood or metal.
- Do not store materials on top of high cabinets where they will be hard to see or reach.
- Do not store corrosive liquids above eye level.
- Provide a specific storage location for each type of chemical, and return the chemicals to those locations after each use.
- **Avoid storing chemicals in the workspace within a laboratory hood, except for those chemicals currently in use.**
- If a chemical does not require a ventilated cabinet, store it inside a closable cabinet or on a shelf that has a lip to prevent containers from sliding off in the event of an accident or fire.
- Do not expose chemicals to heat or direct sunlight.
- Observe all precautions regarding the storage of incompatible chemicals.
- Use corrosion resistant storage trays or secondary containers to collect materials if the primary container breaks or leaks.
- Distinguish between refrigerators used for chemical storage and refrigerators used for food storage. Each refrigerator should be labeled "No Food" or "Food Only".
- Do not store flammable liquids in a refrigerator unless it is approved for such storage. Such refrigerators are designed with non-sparking components to avoid an explosion.

- Chemical storage cabinets located outside the laboratory (e.g., in hallways) should be labeled with the name of the laboratory group that owns and uses it.

1.3.2 Segregation of Chemicals

Incompatible chemicals should not be stored together. Storing chemicals alphabetically, without regard to compatibility, can increase the risk of a hazardous reaction, especially in the event of container breakage.

Use common sense when setting up chemical storage. Segregation that disrupts normal workflow can increase the potential for spills.

There are several possible storage plans for segregation. In general, dry reagents, liquids and compressed gases should be stored separately, then by hazard class, then alphabetically (if desired).

Segregate dry reagents as follows:

- Oxidizing salts
- Flammable solids
- Water-reactive solids
- All other solids

Segregate liquids as follows:

- Acids [Separate mineral acids (hydrochloric, sulfuric) from organic acids (picric, acetic)]
- Bases
- Oxidizers
- Perchlorates
- Flammable or combustible liquids
- All other liquids

Segregate compressed gases as follows:

- Toxic gases
- Flammable gases
- Oxidizing and inert gases

For further information on chemical storage groups and a chemical compatibility chart, refer to Appendix A.

1.3.3 Flammable Liquids

Flammable liquids require special storage considerations. See the Flammable Materials section for more information.

1.3.4 Acids

Mineral acids, including phosphoric, hydrochloric, nitric, sulfuric, and perchloric acid can be stored in a cabinet designed for Corrosive Acids. These non-metallic cabinets have no internal metallic parts, acid resistant coating and a cabinet floor constructed to be

able to contain spillage. Volatile acids, such as nitric or sulfuric acid, should be stored either in a dedicated acid cabinet or in a vented cabinet, particularly after they have been opened. Concentrated mineral acids can be very reactive, even with each other. Concentrated acids can even react vigorously with dilute solutions of the same acid, if mixed together rapidly. For example: concentrated sulfuric acid mixed quickly with 1 molar sulfuric acid will generate a lot of heat. Different concentrated acids should be stored apart. If stored within the same cabinet, plastic trays, tubs or buckets work well to keep different acids apart within the cabinet.

Picric Acid can form explosive salts with many metals, or by itself when dry. Perchloric Acid is an extremely powerful oxidizer and must be kept away from all organic materials, including wood, and may not be stored in a chemical fume hood. See the Corrosives Materials section for more information.

Below is the suggested organization of laboratory acids in secondary containment. Trays may be kept in the same acid cabinet.

| Tray Organization | Acids allowed in Tray | Incompatibilities with the acids in the tray |
|--------------------------------------|---|--|
| Inorganic Acid Tray #1 (Nitric Acid) | Nitric Acid - Nitric Acid is very reactive. It is recommended that it should be separated from all other acids. | All organic acids (e.g. Acetic Acid), Chlorosulfonic Acid, Hydrofluoric Acid, Hydrozoic Acid, Perchloric acid, Phthalic Acid, Salicylic Acid, Sulfamic acid, Sulfuric acid |
| Inorganic Acid Tray #2 | Hydrochloric Acid, Hydrobromic Acid, Chromic Acid, Phosphoric Acid, Chlorosulfonic Acid, Hydriodic Acid | All organic acids (e.g. Acetic Acid), Perchloric Acid, Sulfuric Acid |
| Inorganic Acid Tray #3 | Hydrofluoric Acid - Hydrofluoric Acid is a Highly Acute Toxin and should be stored in a area accessible only by authorized personnel. Relatively small burns from this acid can be lethal. Do not store in glass. Use plastic containers and secondary containment. | All organic acids (e.g. Acetic Acid), Bismuthic acid, Chlorosulfonic acid, Methanesulfonic acid, Nitric acid, Perchloric acid, Sulfuric acid |
| Inorganic Acid Tray #4 | Sulfuric Acid | All organic acids (e.g. Acetic Acid), Chlorosulfonic acid, Hydrochloric acid, Perchloric acid |
| Inorganic Acid #5 | Perchloric Acid | All organic acids (e.g. Acetic Acid), Hydrochloric acid, Hydrofluoric acid, Nitric acid, Oleic acid, o-Periodic acid, Sulfuric acid |
| Organic Acid Tray #1 | All Organic Acids, e.g. Acetic Acid, Formic Acid, Propionic Acid, Butyric Acid, Chloroacetic Acid, Trichloroacetic Acid, Oxalic Acid, Salicylic Acid. | All inorganic (mineral) acids e.g. Chlorosulfonic acid, Chromic Acid, Hydrochloric Acid, Hydrofluoric Acid, Nitric Acid, Perchloric acid, Sulfuric Acid |
| Inorganic Acid Tray #2 | Hydrochloric Acid, Hydrobromic Acid, Chromic Acid, Phosphoric Acid, Chlorosulfonic Acid, Hydriodic Acid | All organic acids (e.g. Acetic Acid), Perchloric Acid, Sulfuric Acid |

1.3.5 Unstable Chemicals

Ethers and some ketones and olefins may form peroxides when exposed to air or light. Since they may have been packaged in an air atmosphere, peroxides can form even if the container has not been opened.

Some chemicals, such as dinitroglycerine and germane, are shock-sensitive, meaning that they can rapidly decompose or explode when struck, vibrated or otherwise agitated. These compounds become more shock-sensitive with age.

For any potentially unstable chemical:

- On the label, write the date the container was received and the date it was opened.
- Discard containers within 6 months of opening them.
- Discard unopened containers after one year, unless an inhibitor was added. If an inhibitor was added, write down the name of the inhibitor and the date it was added on the label.

1.3.6 Compressed Gases

Compressed gases pose a chemical hazard due to the gases themselves and a high energy source hazard due to the great amount of pressure in the cylinder. Large cylinders may weight 130 pounds or more and can pose a crush hazard to hands and feet.

- All cylinders must be secured to a wall, bench or other support structure using a chain or strap. Alternatively, a cylinder stand may be used.
- Segregate cylinders by gas type (e.g., flammable, inert, etc.).
- Store cylinders away from heat sources and extreme weather conditions.

See the Compressed Gas Cylinders section for more information.

1.3.7 Combustible Materials

Common combustible materials, such as paper, wood, corrugated cardboard cartons and plastic labware, if allowed to accumulate, can create a significant fire hazard in the laboratory. Combustible materials not stored in metal cabinets should be kept to a minimum. Store large quantities of such supplies in a separate room, if possible.

1.4 *Spill Kits*

Spill kits are available in all laboratories. These kits are only to be used for incidental or small releases. Defining an incidental release is included in the annual lab safety training. The Lab Supervisor is responsible for stocking and storing the spill kits. Spill kits contain spill pads, goggles, gloves, scoop, and a bag for disposal.

1.5 Chemical Purchasing

- Order only exact amount to be used.
- Purchase chemicals in small bottles for easier management of unused chemicals.
- Establish a centralized purchasing program for your area to monitor chemical purchases and avoid duplicate orders.
- Note any properties that may preclude long term storage, such as organic peroxide formation.
- Use suppliers who can provide quick delivery of small quantities.
- Establish an inventory for the chemicals in your laboratory. Periodically update the inventory as chemicals are used and purchased.
- Dispose of outdated chemicals that no longer hold their original properties.

1.6 Transporting Chemicals

Spills and chemical exposure can occur if chemicals are transported incorrectly, even when moving chemicals from one part of the laboratory to another.

To avoid this type of incident, consider the following:

- Use a bottle carrier, cart or other secondary container when transporting chemicals in breakable containers (especially 250 ml or more) through hallways or between buildings. Secondary containers are made of rubber or plastic, with carrying handle(s), and are large enough to hold the entire contents of the chemical containers in the event of breakage. A variety of such containers are available from laboratory supply catalogs.
- Transport of hazardous chemicals in individual containers exceeding four liters between buildings is strongly discouraged.
- When moving in the laboratory, anticipate sudden backing up or changes in direction by others. If you should stumble or fall while carrying glassware or chemicals, try to project them away from yourself and others.
- The individual transporting the chemical should be knowledgeable about the hazards of the chemical and should know how to handle a spill of the material.
- When transporting compressed gas cylinders, the cylinder should always be strapped in a cylinder cart and the valve protected with a cover cap. Do not attempt to carry or roll cylinders from one area to another.
- Transport chemicals in freight elevators rather than passenger elevators, if available.
- Keep chemicals in their original packing when transporting, if possible.
- Do not transport chemicals between campuses. Each campus should have chemicals delivered directly from the supplier.
- Do not transport chemicals in passenger vehicles or via public transportation.

1.7 Unattended Experiments

Laboratory operations involving hazardous substances are sometimes carried out continuously or overnight with no one present. It is the responsibility of the worker to

design these experiments so as to prevent the release of hazardous substances in the event of interruptions in utility services such as electricity, cooling water, and inert gas.

- Laboratory lights should be left on, and signs should be posted identifying the nature of the experiment and the hazardous substances in use.
- If appropriate, arrangements should be made for other workers to periodically inspect the operation.
- The Lab Hazard Sign posted outside of the door should include contact information for the responsible individual in the event of an emergency.
- Carefully examine how chemicals and apparatus are stored, considering the possibility for fire, explosion or unintended reactions.

1.8 Working Alone

Individuals using hazardous chemicals should not work alone. Another individual capable of coming to the aid of the worker should be in visual or audio contact.

- If working alone is absolutely necessary, the worker should have a phone immediately available and should be in contact with another person (who knows that he or she is being relied upon) at least every 30 minutes.
- If no one from the laboratory is available, contact UPD at 4-6111 and request that the dispatcher check back by phone at regular intervals.
- The laboratory supervisor or PI is responsible for determining whether the work requires special precautions, such as having two people in the same room for particular operations.

1.9 Flammable Materials

1.9.1 Properties of Flammable and Combustible Liquids

Flammable and combustible liquids vaporize and form flammable mixtures with air when in open containers, when leaks occur, or when heated. To control these potential hazards, several properties of these materials, such as volatility, flashpoint, flammable range and auto ignition temperatures must be understood. An explanation of these terms and other properties of flammable liquids is available during the Lab Safety Training. Information on the properties of a specific liquid can be found in that liquid's material safety data sheet (MSDS), or other reference material.

1.9.2 Storage of Flammable and Combustible Liquids

Flammable and combustible liquids should be stored only in approved containers. Approval for containers is based on specifications developed by organizations such as the US Department of Transportation (DOT), OSHA, the National Fire Protection Agency (NFPA) or American National Standards Institute (ANSI). Containers used by the manufacturers of flammable and combustible liquids generally meet these specifications.

1.9.3 Safety Cans and Closed Containers

Many types of containers are required depending on the quantities and classes of flammable or combustible liquids in use. A safety can is an approved container of not more than 5 gallons capacity that has a spring closing lid and spout cover. Safety cans are designed to safely relieve internal pressure when exposed to fire conditions. A closed container is one sealed by a lid or other device so that liquid and vapor cannot escape at ordinary temperatures.

1.9.4 Flammable Liquid Storage Cabinets

A flammable liquid storage cabinet is an approved cabinet that has been designed and constructed to protect the contents from external fires. Storage cabinets are usually equipped with vents, which are plugged by the cabinet manufacturer. Since venting is not required by any code or by the local municipalities and since venting may actually prevent the cabinet from protecting its contents, vents should remain plugged at all times. Storage cabinets must also be conspicuously labeled "FLAMMABLE – KEEP FIRE AWAY".

1.9.5 Refrigerators

Use only those refrigerators that have been designed and manufactured for flammable liquid storage. Standard household refrigerators must not be used for flammable storage because internal parts could spark and ignite. Refrigerators must be prominently labeled as to whether or not they are suitable for flammable liquid storage.

1.9.6 Storage Considerations:

- Quantities should be limited to the amount necessary for the work in progress.
- No more than 10 gallons of flammable and combustible liquids, combined, should be stored outside of a flammable storage cabinet unless safety cans are used. When safety cans are used, up to 25 gallons may be stored without using a flammable storage cabinet.
- Storage of flammable liquids must not obstruct any exit.
- Flammable liquids should be stored separately from strong oxidizers, shielded from direct sunlight, and away from heat sources.

1.9.7 Handling Precautions

The main objective in working safely with flammable liquids is to avoid accumulation of vapors and to control sources of ignition.

Besides the more obvious ignition sources, such as open flames from Bunsen burners, matches and cigarette smoking, less obvious sources, such as electrical equipment, static electricity and gas-fired heating devices should be considered.

Some electrical equipment, including switches, stirrers, motors, and relays can produce sparks that can ignite vapors. Although some newer equipment have spark-free induction motors, the on-off switches and speed controls may be able to produce a spark when they are adjusted because they have exposed contacts. One solution is to

remove any switches located on the device and insert a switch on the cord near the plug end.

Pouring flammable liquids can generate static electricity. The development of static electricity is related to the humidity levels in the area. Cold, dry atmospheres are more likely to facilitate static electricity. Bonding or using ground straps for metallic or non-metallic containers can prevent static generation.

- Control all ignition sources in areas where flammable liquids are used. Smoking, open flames and spark producing equipment should not be used.
- Whenever possible use plastic or metal containers or safety cans.
- When working with open containers, use a laboratory fume hood to control the accumulation of flammable vapor.
- Use bottle carriers for transporting glass containers.
- Use equipment with spark-free, intrinsically safe induction motors or air motors to avoid producing sparks. These motors must meet National Electric Safety Code (US DOC, 1993) Class 1, Division 2, Group C-D explosion resistance specifications. Many stirrers, Variacs, outlet strips, ovens, heat tape, hot plates and heat guns do not conform to these code requirements.
- Avoid using equipment with series-wound motors, since they are likely to produce sparks.
- Do not heat flammable liquids with an open flame. Steam baths, salt and sand baths, oil and wax baths, heating mantles and hot air or nitrogen baths are preferable.
- Minimize the production of vapors and the associated risk of ignition by flashback. Vapors from flammable liquids are denser than air and tend to sink to the floor level where they can spread over a large area.
- Electrically bond metal containers when transferring flammable liquids from one to another. Bonding can be direct, as a wire attached to both containers, or indirect, as through a common ground system.
- When grounding non-metallic containers, contact must be made directly to the liquid, rather than to the container.
- In the rare circumstance that static cannot be avoided, proceed slowly to give the charge time to disperse or conduct the procedure in an inert atmosphere.

1.9.8 Flammable Aerosols

Flammable liquids in pressurized containers may rupture and aerosolize when exposed to heat, creating a highly flammable vapor cloud. As with flammable liquids, these should be stored in a flammable storage cabinet.

1.9.9 Flammable and Combustible Solids

Flammable solids often encountered in the laboratory include alkali metals, magnesium metal, metallic hydrides, some organometallic compounds, and sulfur. Many flammable solids react with water and cannot be extinguished with conventional dry chemical or carbon dioxide extinguishers.

- Ensure Class D extinguishers, e.g., Met-L-X, are available where flammable solids are used or stored.
- Sand can usually be used to smother a fire involving flammable solids. Keep a container of sand near the work area.
- If a flammable, water-reactive solid is spilled onto skin, brush off as much as possible, then flush with copious amounts of water.
- NEVER use a carbon dioxide fire extinguisher for fires involving lithium aluminum hydride (LAH). LAH reacts explosively with carbon dioxide.

1.9.10 Catalyst Ignition

Some hydrogenated catalysts, such as palladium, platinum oxide, and Raney nickel, when recovered from hydrogenation reactions, may become saturated with hydrogen and present a fire or explosion hazard.

- Carefully filter the catalyst.
- Do not allow the filter cake to become dry.
- Place the funnel containing moist catalyst into a water bath immediately.
- Purge gases, such as nitrogen or argon, may be used so that the catalyst can be filtered and handled in an inert atmosphere.

1.10 Peroxide Forming Compounds and Reactives

Certain chemicals can form dangerous peroxides on exposure to air and light. Since they are sometimes packaged in an atmosphere of air, peroxides can form even though the containers have not been opened. Peroxides may detonate with extreme violence when concentrated by evaporation or distillation, when combined with other compounds, or when disturbed by unusual heat, shock or friction. Formation of peroxides in ethers is accelerated in opened and partially emptied containers. Refrigeration will not prevent peroxide formation and stabilizers will only retard formation.

Peroxide formation may be detected by visual inspection for crystalline solids or viscous liquids, or by using chemical methods or specialized kits for quantitative or qualitative analysis. If you suspect that peroxides have formed, do not open the container to test since peroxides deposited on the threads of the cap could detonate. Contact Risk Management immediately for assistance.

1.10.1 Recommended Work Practices

The following recommendations should be followed to control the hazards of peroxides.

- Know the properties and hazards of all chemicals you are using through adequate research and study, including reading the label and MSDS.
- Inventory all chemical storage at least twice a year to detect forgotten items, leaking containers, and those that need to be discarded.
- Identify chemicals that form peroxides or otherwise deteriorate or become more hazardous with age or exposure to air. Label containers with the date received, the date first opened and the date for disposal as recommended by the supplier.

- Minimize peroxide formation in ethers by storing in tightly sealed containers placed in a cool place in the absence of light. Do not store ethers at or below the temperature at which the peroxide freezes or the solution precipitates.
- Choose the size container that will ensure use of the entire contents within a short period of time.
- Visually or chemically check for peroxides of any opened containers before use.
- Clean up spills immediately. The safest method is to absorb the material onto vermiculite or a similar loose absorbent.
- When working with peroxidizable compounds, wear impact-resistant safety eyewear and face shields. Visitor specs are intended only for slight and brief exposure, and should not be used when working with peroxidizable compounds.
- Do not use solutions of peroxides in volatile solvents under conditions in which the solvent might be vaporized. This could increase the concentration of peroxide in the solution.
- Do not use metal spatulas or magnetic stirring bars (which may leach out iron) with peroxide forming compounds, since contamination with metals can lead to explosive decomposition. Ceramic, Teflon or wooden spatulas and stirring blades are usually safe to use.
- Do not use glass containers with screw-top lids or glass stoppers. Polyethylene bottles with screw-top lids may be used.

1.10.2 Examples of Peroxidizable Compounds

| | |
|--|--|
| <i>Peroxide Hazard on Storage: Discard After Three Months</i> | |
| Divinyl acetylene Divinyl ether Isopropyl ether | Potassium metal Sodium amide Vinylidene chloride |
| <i>Peroxide Hazard on Concentration: Discard After One Year</i> | |
| Acetal Cumene Cyclohexene Cycloxyene Cyclopentene Diacetylene Dicyclopentadiene Diethyl ether Diethylene glycol dimethyl ether (diglyme) | Dioxane Ethylene glycol dimethyl ether (glyme) Furan Methyl acetylene Methylcyclopentane Methyl isobutyl ketone Tetrahydronaphtalene (Tetralin) Tetrahydrofuran Vinyl ethers |
| <i>Hazardous Due to Peroxide Initiation of Polymerization*: Discard After One Year</i> | |
| Acrylic acid Acrylonitrile Butadiene Chloroprene Chlorotrifluoroethylene Methyl methacrylate | Styrene Tetrafluoroethylene Vinyl acetylene Vinyl acetate Vinyl chloride Vinyl pyridine |

* Under storage conditions in the liquid state the peroxide-forming potential increases and certain of these monomers (especially butadiene, chloroprene, and tetrafluoroethylene) should be discarded after three months.

1.10.3 Detection of Peroxides

If there is any suspicion that peroxide is present, do not open the container or otherwise disturb the contents. Call Risk Management for disposal. The container and its contents must be handled with extreme care. If solids, especially crystals, for example, are observed either in the liquid or around the cap, peroxides are most likely present.

If no peroxide is suspected but the chemical is a peroxide former, the following procedures can detect most peroxides.

- Prepare reagent by adding 100 mg sodium iodide (NaI) or potassium iodide (KI) crystals to 1.0 ml of glacial acetic acid. Add 0.5 to 1.0 ml of material being tested to an equal volume of reagent. A yellow color indicates a low concentration (~0.1 per cent) and brown a high concentration of peroxide in the sample. A blank should be run, using some non-peroxidizable compound such as pure n-hexane.
- Peroxide test strips, which change color to indicate the presence of peroxides, may be purchased through most laboratory reagent distributors. For proper operation, the strips must be air-dried until the solvent evaporates and then exposed to moisture.

1.11 **Corrosive Materials**

Many chemicals commonly used in the laboratory are corrosive or irritating to body tissue. They present a hazard to the eyes and skin by direct contact, to the respiratory tract by inhalation or to the gastrointestinal system by ingestion.

1.11.1 Corrosive Liquids

Corrosive liquids (e.g. mineral acids, alkali solutions and some oxidizers) represent a very significant hazard because skin or eye contact can readily occur from splashes and their effect on human tissue generally takes place very rapidly. Bromine, sodium hydroxide, sulfuric acid and hydrogen peroxide are examples of highly corrosive liquids.

The following should be considered:

- The eyes are particularly vulnerable. It is therefore essential that approved eye and face protection be worn in all laboratories where corrosive chemicals are handled.
- Gloves and other chemically resistant protective clothing should be worn to protect against skin contact.
- To avoid a flash steam explosion due to the large amount of heat evolved, always add acids or bases to water (and not the reverse).
- Acids and bases should be segregated for storage.
- Liquid corrosives should be stored below eye level.
- Adequate quantities of spill control materials should be readily available. Specialized spill kits for acids and bases are available through most chemical and laboratory safety supply catalogs.

1.11.2 Corrosive Gases and Vapors

Corrosive gases and vapors are hazardous to all parts of the body; certain organs (e.g. the eyes and the respiratory tract) are particularly sensitive. The magnitude of the effect is related to the solubility of the material in the body fluids. Highly soluble gases (e.g. ammonia, hydrogen chloride) cause severe nose and throat irritation, while substances of lower solubility (e.g. nitrogen dioxide, phosgene, sulfur dioxide) can penetrate deep into the lungs.

- Warning properties such as odor or eye, nose or respiratory tract irritation may be inadequate with some substances. Therefore, they should not be relied upon as a warning of overexposure.
- Perform manipulations of materials that pose an inhalation hazard in a chemical fume hood to control exposure or wear appropriate respiratory protection.
- Protect all exposed skin surfaces from contact with corrosive or irritating gases and vapors.
- Regulators and valves should be closed when the cylinder is not in use and flushed with dry air or nitrogen after use.
- When corrosive gases are to be discharged into a liquid, a trap, check valve, or vacuum break device should be employed to prevent dangerous reverse flow.

1.11.3 Corrosive Solids

Corrosive solids, such as sodium hydroxide and phenol, can cause burns to the skin and eyes. Dust from corrosive solids can be inhaled and cause irritation or burns to the respiratory tract. Many corrosive solids, such as potassium hydroxide and sodium hydroxide, can produce considerable heat when dissolved in water.

- Wear gloves and eye protection when handling corrosive solids.
- When mixing with water, always slowly add the corrosive solid to water, stirring continuously. Cooling may be necessary.
- If there is a possibility of generating a significant amount of dust, conduct work in a fume hood.

1.12 **Compressed Gases**

Compressed gases can be toxic, flammable, oxidizing, corrosive, inert or a combination of hazards. In addition to the chemical hazards, compressed gases may be under a great deal of pressure. The amount of energy in a compressed gas cylinder makes it a potential rocket. Appropriate care in the handling and storage of compressed gas cylinders is essential.

1.12.1 Hazards

The following is an overview of the hazards to be avoided when handling and storing compressed gases:

- **Asphyxiation:** Simple asphyxiation is the primary hazard associated with *inert gases*. Because inert gases are colorless and odorless, they can escape into the atmosphere undetected and quickly reduce the concentration of oxygen below the level necessary to support life. The use of oxygen monitoring equipment is strongly recommended for enclosed areas where inert gases are being used.

- **Fire and Explosion:** Fire and explosion are the primary hazards associated with *flammable gases, oxygen and other oxidizing gases*. Flammable gases can be ignited by static electricity or by a heat source, such as a flame or a hot object. Oxygen and other oxidizing gases do not burn, but will support combustion of organic materials. Increasing the concentration of an oxidizer accelerates the rate of combustion. Materials that are nonflammable under normal conditions may burn in an oxygen-enriched atmosphere.
- **Chemical Burns:** *Corrosive gases* can chemically attack various materials, including fire-resistant clothing. Some gases are not corrosive in their pure form, but can become extremely destructive if a small amount of moisture is added. Corrosive gases can cause rapid destruction of skin and eye tissue.
- **Chemical Poisoning:** Chemical poisoning is the primary hazard of *toxic gases*. Even in very small concentrations, brief exposure to these gases can result in serious poisoning injuries. Symptoms of exposure may be delayed.
- **High Pressure:** All compressed gases are potentially hazardous because of the high pressure stored inside the cylinder. A sudden release of pressure can cause injuries by propelling a cylinder or whipping a line.
- **Cylinder Weight:** A full size cylinder may weigh more than 130 pounds. Moving a cylinder manually may lead to back or muscle injury. Dropping or dragging a cylinder could cause serious injury.

1.12.2 Handling Precautions

- Avoid dropping, dragging or sliding cylinders. Use a suitable hand truck or cart equipped with a chain or belt for securing the cylinder to the cart, even for short distances.
- Do not permit cylinders to strike each other violently. Cylinders should not be used as rollers for moving material or other equipment.
- Cylinder caps should be left on each cylinder until it has been secured against a wall or bench or placed in a cylinder stand, and is ready for installation of the regulator. Cylinder caps protect the valve on top of the cylinder from damage if knocked.
- Never tamper with pressure relief devices in valves or cylinders.
- Use only wrenches or tools provided by the cylinder supplier to remove a cylinder cap or to open a valve. Never use a screwdriver or pliers.
- Keep the cylinder valve closed except when in use.
- Position cylinders so that the cylinder valve is accessible at all times.
- Use compressed gases only in a well-ventilated area. Toxic, flammable and corrosive gases should be carefully handled in a hood or gas cabinet. Proper containment systems should be used and minimum quantities of these products should be kept on-site.
- When discharging gas into a liquid, a trap or suitable check valve should be used to prevent liquid from getting back into the cylinder or regulator.
- Where more than one type of gas is in use, label gas lines. This is particularly important when the gas supply is not in the same room or area as the operation using the gases.
- Do not use the cylinder valve itself to control flow by adjusting the pressure.

1.12.3 Storage of Compressed Gas Cylinders

- All cylinders must be secured to a wall, bench or fixed support using a chain or strap placed 2/3 of the way up. Cylinder stands are an alternative to straps.
- Cylinders should be strapped individually.
- Do not store full and empty cylinders together.
- Oxidizers and flammable gases should be stored in areas separated by at least 20 feet or by a noncombustible wall.
- Cylinders should not be stored near radiators or other heat sources. If storage is outdoors, protect cylinders from weather extremes and damp ground to prevent corrosion.
- No part of a cylinder should be subjected to a temperature higher than 125°F. A flame should never be permitted to come in contact with any part of a compressed gas cylinder.
- Do not place cylinders where they may become part of an electric circuit.
- Keep the number of cylinders in a laboratory to a minimum to reduce the fire and toxicity hazards.
- Lecture bottles should always be returned to the distributor or manufacturer promptly when no longer needed or discarded if at atmospheric pressure.
- Ensure that the cylinder is properly and prominently labeled as to its contents.
- NEVER place acetylene cylinders on their side.

1.12.4 Using Compressed Gas Cylinders

Before using cylinders, read all label information and material safety data sheets (MSDSs) associated with the gas being used. The cylinder valve outlet connections are designed to prevent mixing of incompatible gases. The outlet threads vary in diameter; some are internal and some are external; some are right-handed and some are left-handed. Generally, right-handed threads are used for fuel gases.

To set up and use the cylinder, follow these steps:

1. Attach the closed regulator to the cylinder. **Never open the cylinder valve unless the regulator is completely closed.** Regulators are specific to the gas involved. A regulator should be attached to a cylinder without forcing the threads. If the inlet of a regulator does not fit the cylinder outlet, no effort should be made to try to force the fitting. A poor fit may indicate that the regulator is not intended for use on the gas chosen.
2. Turn the delivery pressure adjusting screw counter-clockwise until it turns freely. This prevents unintended gas flow into the regulator.
3. Open the cylinder **slowly** until the inlet gauge on the regulator registers the cylinder pressure. If the cylinder pressure reading is lower than expected, the cylinder valve may be leaking.
4. With the flow control valve at the regulator outlet closed, turn the delivery pressure adjusting screw clockwise until the required delivery pressure is reached.
5. Check for leaks using *Snoop* or soap solution. At or below freezing temperatures, use a glycerin and water solution, such as *Snoop*, rather than soap. Never use an open flame to detect leaks.

6. When finished with the gas, close the cylinder valve and release the regulator pressure.

1.12.5 Assembly of Equipment and Piping

- Do not force threads that do not fit exactly.
- Use Teflon tape or thread lubricant for assembly. Teflon tape should only be used for tapered pipe thread, not straight lines or metal-to-metal contacts.
- Avoid sharp bends of copper tubing. Copper tubing hardens and cracks with repeated bending.
- Inspect tubing frequently and replace when necessary.
- Tygon and plastic tubing are not appropriate for most pressure work. These materials can fail under pressure or thermal stress.
- Do not mix different brands and types of tube fittings. Construction parts are usually not interchangeable.
- Do not use oil or lubricants on equipment used with oxygen.
- Do not use copper piping for acetylene.
- Do not use cast iron piping for chlorine.

1.12.6 Leaking Cylinders

Most leaks occur at the valve in the top of the cylinder and may involve the valve threads valve stem, valve outlet, or pressure relief devices. Lab personnel should not attempt to repair leaking cylinders.

Where action can be taken without serious exposure to lab personnel:

1. Move the cylinder to an isolated, well-ventilated area (away from combustible materials if the cylinder contains a flammable or oxidizing gas).
2. Contact UPD at 4-6111 on the Foggy Bottom campus and 2-6111 on the Mount Vernon campus.

Whenever a large or uncontrollable leak occurs, evacuate the area and immediately contact UPD at 4-6111 on the Foggy Bottom campus and 2-6111 on the Mount Vernon campus.

1.12.7 Empty Cylinders

- Remove the regulator and replace the cylinder cap.
- Mark the cylinder as empty or MT and store in a designated area for return to the supplier.
- Do not store full and empty cylinders together.
- Do not have full and empty cylinders connected to the same manifold. Reverse flow can occur when an empty cylinder is attached to a pressurized system.
- Do not refill empty cylinders. Only the cylinder supplier should refill gases.
- Do not empty cylinders to a pressure below 25 psi (172 Kpa). The residual contents may become contaminated with air.
- Lecture bottles should always be returned to the distributor or manufacturer promptly when no longer needed. Do not purchase lecture bottles that cannot be returned.

1.12.8 Flammable Gases

The storage of flammable gas cylinders is limited to two (2) type 1 (10" x 50") cylinders per 500 square feet of unsprinklered laboratory space. Liquefied flammable gas containers should be limited to two (2) 9" x 30" cylinders per 500 square feet of unsprinklered laboratory space or three (3) 9" x 30" cylinders per 500 square feet of **sprinkled** laboratory space.

- Keep sources of ignition away from the cylinders.
- Oxidizers and flammable gases should be stored in areas separated by at least 20 feet or by a non-combustible wall.
- Bond and ground all cylinders, lines and equipment used with flammable compressed gases.

1.13 **Appendix A: Chemical Storage Groups**

In this plan there are nine storage groups. Seven of these groups cover storage of liquids because of the wide variety of hazards posed by these chemicals. Specific instructions must be followed for metal hydrides (Group VIII) and certain individual compounds, but otherwise, dry solids are in Group IX.

Many liquid chemicals pose hazards that correspond to more than one storage group. These chemicals should be stored in the lowest group number.

| | |
|------------|-----------------------------|
| Group I | Flammable Liquids |
| Group II | Poisons - volatile |
| Group III | Acids - Oxidizing |
| Group IV | Acids - Organic and Mineral |
| Group V | Bases - Liquid |
| Group VI | Oxidizer - Liquid |
| Group VII | Poisons - Non-volatile |
| Group VIII | Reactives |
| Group IX | Solids |

1.13.1 Storage Group Definitions

Group I: Flammable Liquids

Includes liquids with flashpoints < 100 F. Examples: all alcohols, acetone, acetaldehyde, acetonitrile, amyl acetate, benzene, cyclohexane, dimethyldichlorosilane, dioxane, ether, ethyl acetate, histoclad, hexane, hydrazine, methyl butane, picolene, piperidine, propanol, pyridine, scintillation liquids, all silanes, tetrahydrofuran, toluene, triethylamine, xylene.

- Primary Storage Concern: To protect from ignition.
- Recommended Facilities/Measures:
 - o Flammable cabinet

- Compatible Storage Groups: Volatile poisons may be in the same compartment of the flammable cabinet as flammables if bases are not present.

Group II: Volatile Poisons

Includes poisons, toxics and known and suspected carcinogens with strong odor or evaporation rate greater than 1 (butyl acetate = 1): Examples: carbon tetrachloride, chloroform, dimethylformamide, dimethyl sulfate, formamide, formaldehyde, halothane, mercaptoethanol, methylene chloride, phenol.

- Primary Storage Concern: To prevent inhalation exposures.
- Recommended Facilities/Measures:
 - Flammable cabinet
- Compatible Storage Groups: Volatile poisons may be in the same compartment of the flammable cabinet as flammable if bases are not present.

Group III: Oxidizing Acids

All oxidizing acids are highly reactive with most substances and each other. Examples: nitric, sulfuric, perchloric, phosphoric acids, and chromic acids.

- Primary Storage Concern: Preventing contact and reaction with each other and other substances and corrosive action on surfaces.
- Recommended Facilities/Measures:
 - Safety Cabinet. Each oxidizing acid must be double-contained, i.e., the primary container must be kept inside canister, tray or tub.
 - In tubs or trays in normal cabinet.
- Compatible Storage Groups: Oxidizing acids must be double-contained and should be segregated in their own compartment in a safety cabinet. When quantities are small (e.g., less than four gallons) they do not warrant a separate compartment. Small quantities may be double-contained and stored with Group 4 Organic and Mineral Acids. Store oxidizing acids on bottom shelf below Group 4.

Group IV: Organic and Mineral Acids

Examples: acetic, butyric, formic, glacial acetic, hydrochloric, isobutyric, mercaptopropionic, propionic, trifluoroacetic acids.

- Primary Storage Concern: To prevent contact and reaction with bases and oxidizing acids and corrosive action on surfaces.
- Recommended Facilities/Measures:
 - Safety cabinet.
 - In tubs or trays in normal cabinet.
- Compatible Storage Groups: Small amount (e.g., less than four gallons) of double-contained oxidizing acids can be stored in the same compartment with organic acids if the oxidizing acids are stored on the bottom shelf. Exceptions: acetic anhydride and trichloroacetic anhydride are corrosive. These acids are very reactive with other acids and should not be stored in this group. It is better to store these with organic compounds as in Group 7 Non-volatile Liquid Poisons.

Group V: Liquid Bases

Examples: sodium hydroxide, ammonium hydroxide, calcium hydroxide, glutaraldehyde.

- Primary Storage Concern: Preventing contact and reaction with acids.
- Recommended Facilities/Measures:
 - Safety cabinet.
 - In tubs or trays in normal cabinet.
- Compatible Storage Groups: Liquid bases may be stored with flammables in the flammable cabinet if volatile poisons are not also stored there.

Group VI: Oxidizing liquids

Oxidizing liquids react with everything potentially causing explosions or corrosion of surfaces. Examples: ammonium persulfate, hydrogen peroxide (if greater than or equal to 30%).

- Primary Storage Concern: To isolate from other materials.
- Recommended Facilities/Measures:
 - Total quantities exceeding 3 liters should be kept in a cabinet housing no other chemicals.
 - Smaller quantities must be double-contained if kept near other chemicals.
- Compatible Storage Groups: None.

Group VII: Non-Volatile Liquid Poisons

Includes highly toxic (LD50 oral rat < 50 mg/kg) and toxic chemicals (LD50 oral rat < 500 mg/kg), known carcinogens, suspected carcinogens and mutagens. Examples: acrylamide solutions; diethylpyrocarbonate; diisopropyl fluorophosphate; uncured epoxy resins; ethidium bromide; triethanolamine.

- Primary Storage Concern: To prevent contact and reaction with other substances.
- Recommended Facilities/Measures:
 - Cabinet or refrigerator (i.e., must be enclosed).
 - Do not store on open shelves in the lab or cold room.
 - Liquid poisons in containers larger than 1 liter must be stored below bench level on shelves closest to the floor. Smaller container of liquid poison can be stored above bench level only if behind sliding (non-swinging) doors.
- Compatible Storage Groups: Non-hazardous liquids (e.g., buffer solutions). Exceptions: Anhydrides, e.g., acetic and trichloroacetic, are organic acids, however it is better to store with this group than with Group 4 Organic Acids, since they are highly reactive with other organic or mineral acids.

Group VIII: Reactives Metal Hydrides and Pyrophorics

Most metal hydrides react violently with water, some ignite spontaneously in air (pyrophoric). Examples of metal hydrides, are sodium borohydride, calcium hydride, lithium aluminum hydride. Other pyrophorics are boron, diborane, dichloroborane, 2-Furaldehyde, diethyl aluminum chloride, lithium, white or yellow phosphorus and trimethyl aluminum. Other water reactives include aluminum chloride-anhydrous,

calcium carbide, acetyl chloride, chlorosulonic acid, sodium, potassium, phosphorous pentachloride calcium, aluminum tribromide, calcium oxide, and acid anhydrides.

- Primary Storage Concern: To prevent contact and reaction with liquids and, in some cases, air.
- Recommended Facilities/Measures:
 - o Secure, water-proof double-containment according to label instructions.
 - o Isolation from other storage groups.
- Compatible Storage Groups: If securely double-contained to prevent contact with water and/or air, metal hydrides may be stored in the same area as Group 9 Dry Solids.

Group IX: Dry Solids

Includes all powders, hazardous and non-hazardous. Examples: benzidine, cyanogen bromide, ethylmaleimide, oxalic acid, potassium cyanide, sodium cyanide.

- Primary Storage Concern: To prevent contact and potential reaction with liquids.
- Recommended Facilities/Measures:
 - o Cabinets are recommended, but if not available, open shelves are acceptable.
 - o Store above liquids.
 - o Warning labels on highly toxic powders should be inspected and highlighted or amended if they do not cause the containers to stand out against less toxic substances in this group.
 - o It is recommended that the most hazardous substances in this group be segregated.
 - o It is particularly important to keep liquid poisons below cyanide-or sulfide-containing poisons (solids). A spill of aqueous liquid onto cyanide - or sulfide - containing poisons would cause a reaction that would release poisonous gas.
- Compatible Storage Groups: Metal hydrides, if properly double-contained may be stored in the same area. Exceptions: Solid picric or picric sulfonic acid can be stored with this group, but should be checked regularly for dryness. When completely dry, picric acid is explosive and may detonate upon shock or friction. Picric acid in contact with some metals may form explosive metal picrates. Use non-metal caps.

1.13.2 Chemical Incompatibility Chart

Mixing these chemicals purposely or as a result of a spill can result in heat, fire, explosion, and/or toxic gases. This is a partial list.

| | |
|--|--|
| Acetic Acid | Chromic Acid, nitric acid, hydroxyl-containing compounds, ethylene glycol, perchloric acid, peroxides, and permanganates. |
| Acetone | Bromine, chlorine, nitric acid, sulfuric acid, and hydrogen peroxide. |
| Acetylene | Bromine, chlorine, copper, mercury, fluorine, iodine, and silver. |
| Alkaline and Alkaline Earth Metals such as calcium, lithium, magnesium, sodium, potassium, powdered aluminum | Carbon dioxide, carbon tetrachloride and other chlorinated hydrocarbons, water, Bromine, chlorine, fluorine, and iodine. Do not use CO ₂ , water or dry chemical extinguishers. Use Class D extinguisher (e.g., Met-L-X) or dry sand. |
| Aluminum and its Alloys (especially powders) | Acid or alkaline solutions, ammonium persulfate and water, chlorates, chlorinated compounds, nitrates, and organic compounds in nitrate/nitrate salt baths. |
| Ammonia (anhydrous) | Bromine, chlorine, calcium hypochlorite, hydrofluoric acid, iodine, mercury, and silver. |
| Ammonium Nitrate | Acids, metal powders, flammable liquids, chlorates, nitrates, sulfur and finely divided organics or other combustibles. |
| Aniline | Hydrogen peroxide or nitric acid. |
| Bromine | Acetone, acetylene, ammonia, benzene, butadiene, butane and other petroleum gases, hydrogen, finely divided metals, sodium carbide, turpentine. |
| Calcium Oxide | Water |
| Carbon (activated) | Calcium hypochlorite, all oxidizing agents. |
| Caustic (soda) | Acids (organic and inorganic). |
| Chlorates or Perchlorates | Acids, aluminum, ammonium salts, cyanides, phosphorous, metal powders, oxidizable organics or other combustibles, sugar, sulfides, and sulfur. |
| Chlorine | Acetone, acetylene, ammonia, benzene, butadiene, butane and other petroleum gases, hydrogen, finely divided metals, sodium carbide, turpentine. |
| Chlorine Dioxide | Ammonia, methane, phosphine, hydrogen sulfide. |
| Chromic Acid | Acetic acid, naphthalene, camphor, alcohol, glycerine, turpentine and other flammable liquids. |
| Copper | Acetylene, hydrogen peroxide. |
| Cumene Hydroperoxide | Acids |
| Cyanides | Acids |
| Flammable Liquids | Ammonium nitrate, chromic acid, hydrogen peroxide, nitric acid, sodium peroxide, bromine, chlorine, fluorine, iodine. |
| Fluorine | Isolate from everything. |
| Hydrazine | Hydrogen peroxide, nitric acid, and other oxidizing agents. |
| Hydrocarbons | Bromine, chlorine, chromic acid, fluorine, hydrogen peroxide, and sodium peroxide. |

| | |
|---------------------------------|---|
| Hydrocyanic Acid | Nitric acid, alkali. |
| Hydrofluoric Acid | Ammonia, aqueous or anhydrous. |
| Hydrogen Peroxide (anhydrous) | Chromium, copper, iron, most metals or their salts, aniline, any flammable liquids, combustible materials, nitromethane, and all other organic material. |
| Hydrogen Sulfide | Fuming nitric acid, oxidizing gases. |
| Iodine | Acetylene, ammonia (aqueous or anhydrous), hydrogen. |
| Mercury | Acetylene, alkali metals, ammonia, fulminic acid, nitric acid with ethanol, hydrogen, oxalic acid. |
| Nitrates | Combustible materials, esters, phosphorous, sodium acetate, stannous chloride, water, zinc powder. |
| Nitric acid (concentrated) | Acetic acid, acetone, alcohol, aniline, chromic acid, flammable gases and liquids, hydrocyanic acid, hydrogen sulfide and nitratable substances. |
| Nitrites | Potassium or sodium cyanide. |
| Nitroparaffins | Inorganic bases, amines. |
| Oxalic acid | Silver, mercury, and their salts. |
| Oxygen (liquid or enriched air) | Flammable gases, liquids, or solids such as acetone, acetylene, grease, hydrogen, oils, phosphorous. |
| Perchloric Acid | Acetic anhydride, alcohols, bismuth and its alloys, paper, wood, grease, oils or any organic materials and reducing agents. |
| Peroxides (organic) | Acid (inorganic or organic). Also avoid friction and store cold. |
| Phosphorus (white) | Air, oxygen. |
| Phosphorus pentoxide | Alcohols, strong bases, water. |
| Potassium | Air (moisture and/or oxygen) or water, carbon tetrachloride, carbon dioxide. |
| Potassium Chlorate | Sulfuric and other acids. |
| Potassium Perchlorate | Acids. |
| Potassium Permanganate | Benzaldehyde, ethylene glycol, glycerol, sulfuric acid. |
| Silver and silver salts | Acetylene, oxalic acid, tartaric acid, fulminic acid, ammonium compounds. |
| Sodium | See Alkali Metals |
| Sodium Chlorate | Acids, ammonium salts, oxidizable materials and sulfur. |
| Sodium Nitrite | Ammonia compounds, ammonium nitrate, or other ammonium salts. |
| Sodium Peroxide | Any oxidizable substances, such as ethanol, methanol, glacial acetic acid, acetic anhydride, benzaldehyde, carbon disulfide, glycerol, ethylene glycol, ethyl acetate, methyl acetate, furfural, etc. |
| Sulfides | Acids. |
| Sulfur | Any oxidizing materials. |
| Sulfuric Acid | Chlorates, perchlorates, permanganates, compounds with light metals such as sodium, lithium, and potassium. |
| Water | Acetyl chloride, alkaline and alkaline earth metals, their hydrides and oxides, barium peroxide, carbides, chromic acid, phosphorous oxychloride, phosphorous pentachloride, phosphorous pentoxide, sulfuric acid, sulfur trioxide. |