HAZARDOUS MATERIALS

INTRODUCTION

PURPOSE

Duke University (including Duke Medicine facilities) shall take all reasonable precautions to protect its employees, patients, students, and property against the danger of hazardous materials. This policy presents information regarding the safety, procurement, handling, storage and use of hazardous materials not covered in other sections. Other applicable chapters and supplements in the Duke University Safety Manual should be consulted for information regarding asbestos, bloodborne pathogens, hazardous drugs, hazard communication, reproductive hazards, and waste management. Additional information specific to laboratory locations is covered under the Duke Laboratory Safety Manual. Radioactive materials are covered in the Duke Radiation Safety Manual.

DEFINITIONS

Acutely Toxic – A chemical is acutely toxic if it causes adverse effects following an inhalation exposure of 4 hours; or oral or dermal administration of a single dose, or multiple doses given within 24 hours.

Aspiration Hazard – A material that causes pulmonary injury or death when inhaled directly through the oral or nasal cavity, or indirectly from vomiting, into the trachea and lower respiratory system.

Carcinogen – A chemical that induces cancer or increases its incidence.

Combustible Liquid – A flammable liquid designated by the North Carolina Fire Code as having a flash point at or above 100°F. Combustible liquids are divided into subclasses as follows:

Class	Flashpoint (Closed Cup)
II	At or above 100 but below 140°F.
IIIA	At or above 140 but below 200°F.
IIIB	At or above 200°F.

Corrosive - A chemical is considered to be corrosive if it causes irreversible damage to the skin; namely, visible necrosis through the epidermis and into the dermis, following the

application of a test substance for up to 4 hours. This term is also applied to materials which by chemical action will materially damage metals.

Cryogens - Cryogens are gases which have been cooled to the point of liquefaction or solidification that have a boiling point below -200°F. In addition to their ability to freeze tissue, they may also present toxicity, flammability, or other hazards. Commonly used cryogens include liquid nitrogen, liquid helium, liquid argon, and solid carbon dioxide (dry ice).

DHS Chemicals of Interest – A list of chemicals regulated by the federal Department of Homeland Security (DHS) because of their potential use in terrorism. Appendix A of the Chemical Facility Anti-Terrorism Standard (CFATS) lists threshold quantities for each chemical of interest for theft, sabotage, and release.

Explosive – a solid or liquid chemical which is in itself capable by chemical reaction of producing gas at such a temperature and pressure and at such a speed as to cause damage to the surroundings. Pyrotechnic chemicals are included even when they do not evolve gases.

Flammable Gas – A gas having a flammable range with air at a temperature of 20°C (68°F) and a standard pressure of 101.3 kPa (14.7 psi).

Flammable Liquid – As designated by the North Carolina Fire Code, Flammable liquids are liquids having a flashpoint below 100°F. Flammable liquids are also known as Class I liquids and are divided into subclasses as follows:

Class	Flashpoint (Closed Cup)	Boiling Point
IA	Below 73°F.	Below 100°F.
IB	Below 73°F.	100°F or above.
IC	73-99°F.	

As classified by OSHA under the GHS system there are 4 categories of Flammable Liquids as follows:

Category	Criteria
1	Flash point <23 °C (73.4 °F) and initial boiling point ≤35 °C (95 °F).
2	Flash point <23 °C (73.4 °F) and initial boiling point >35 °C (95 °F).
3	Flash point ≥23 °C (73.4 °F) and ≤60 °C (140 °F).
4	Flash point >60 °C (140 °F) and ≤93 °C (199.4 °F).

Flammable Solid - powdered, granular, or pasty chemicals which are dangerous if they can be easily ignited by brief contact with an ignition source, such as a burning match, and if the flame spreads rapidly, or which may cause or contribute to fire through friction. Flammable solids include materials which, in contact with water, emit flammable gases.

Gases Under Pressure - A gas under pressure is any gas contained in a receptacle at a pressure of 200 kPa (29 psi) gauge or more, or which are liquefied or liquefied and refrigerated. They include compressed gases, liquefied gases, dissolved gases, and refrigerated liquefied gases.

Globally Harmonized System of Classification and Labeling of Chemicals (GHS) – The United Nations system of classification of health, physical and environmental hazards, as well as specifying what information should be included on labels of hazardous chemicals as well as safety data sheets.

Mutagens – Chemicals that cause a permanent change in the amount or structure of genetic material in cells.

Nanomaterials - Materials having one or more external dimensions, or an internal structure of 100 nm or less, which could exhibit novel characteristics compared to the same material without nanoscale features.

Organic Peroxides – Organic compounds that contain the bivalent -O-O-structure and which may be considered to be a structural derivative of hydrogen peroxide where one or both of the hydrogen atoms has been replaced by an organic radical. The term organic peroxide includes organic peroxide mixtures containing at least one organic peroxide. Organic peroxides are thermally unstable chemicals, which may undergo exothermic self-accelerating decomposition.

Oxidizers – Chemicals other than blasting agents or explosives that initiate or promote combustion in other materials, thereby causing fire either of themselves or through the release of oxygen or other gases.

Pyrophoric Materials – A chemical which, even in small quantities, is liable to ignite within five minutes of coming into contact with air. Self-heating chemicals differ from pyrophoric chemicals in that they will ignite only in large amounts and after long periods of time.

Reproductive Toxins – Chemicals which adversely affect sexual function and fertility in adult males and females, as well as development of the offspring.

Sensitizers - a chemical that will lead to hypersensitivity of the airways following inhalation of the chemical or an allergic response following skin contact.

Self-Reactive Chemicals – Thermally unstable liquid or solid chemicals liable to undergo a strongly exothermic decomposition even without participation of oxygen (air).

Sensitizer - Chemicals that causes an allergic response following skin contact or airway hypersensitivity following inhalation. Sensitization includes two phases: induction caused by the initial exposure, and elicitation of follow-up responses, which may be more severe.

Target Organ Toxicity – Non-lethal damage to a specific organ following a single or repeated exposure.

RESPONSIBILITIES

Departments shall:

- Ensure full compliance with the detailed responsibilities of employees, set forth below, and in any department-specific or entity-specific (e.g., hospital-specific) policies or procedures applicable to their work areas.
- Ensure that cylinders and containers supplied by vendors meet the applicable standards.
- Ensure that proper storage areas are provided.
- Refuse delivery of chemicals and cylinders to areas where storage facilities do not meet requirements.
- Post hazardous material storage areas with appropriate caution signs.
- Ensure that hazardous materials are transported in a safe manner and in accordance with applicable regulations.
- Ensure, for laboratory work areas, that quantities of DHS Chemicals of Interest are reported to OESO annually by responsible persons.

Employees shall:

- Use proper procedures when working with hazardous materials.
- Use available engineering controls and personal protective equipment as appropriate.
- Transport hazardous materials in a safe manner.
- Store hazardous materials in proper containers and in areas specifically designated.

OESO shall:

- Assist departments in evaluating hazardous material use and storage.
- Review renovation or construction designs to assess adequacy of planned storage.
- Conduct audits of hazardous material use, storage, and disposal.

PROCEDURES

Hazardous material usage, handling, storage, and disposal should be appropriate for the hazards and applicable regulations associated with each material class. Specific classes are discussed in detail below.

Use a hierarchy of controls that places emphasis on keeping hazards out of the workplace when possible. First, consider eliminating the hazardous material or substituting safer alternatives. When use of hazardous chemicals is necessary, the preferred controls are those which remove the hazard from the workplace or place a barrier between the worker and the hazard (engineering controls) followed by work practices, and personal protective equipment (PPE), which require more effort on the part of the individual employee.

Where a hazard assessment has indicated that PPE is necessary, use the appropriate PPE to prevent contact with skin and mucous membranes. For additional information on PPE requirements and selection, refer to Chapter 1 of this Section, entitled “Personal Protective Equipment” and the accompanying Supplement X entitled “PPE Selection Guidelines and Quick Reference Guide”.

For all hazardous chemicals, labeling should be done in accordance with OSHA’s Hazard Communication standard (available as Supplement L to this Manual) and Section V, Chapter 2

of this Manual entitled “Hazard Communication”.

For DHS Chemicals of Interest, manage inventory to minimize quantities on hand so that aggregate quantities of these chemicals can remain below thresholds published in Appendix A of the Chemical Facilities Anti-Terrorism Standard (CFATS). In particular, quantities of nitric acid and thiodiglycol should be minimized. When DHS Chemicals of Interest are used, the quantities on hand must be accurately reported.

FLAMMABLE LIQUIDS

HAZARDS

Fire is the main hazard associated with flammable liquids; however, individual chemicals may have associated health hazards.

STORAGE OUTSIDE OF BUILDINGS

Suitable fire control devices, such as portable fire extinguishers, shall be available at locations where flammable liquids are stored. Contact OESO for installation of appropriate devices.

Open flames and smoking shall not be permitted in flammable liquid storage areas. "No Smoking" and "No Open Flames" signs shall be conspicuously posted in these areas.

INSIDE STORAGE

Flammable liquids shall not be stored in a manner that hinders the safe egress of people. The OESO Fire Safety division shall be consulted for determination of whether or not the aggregate quantity of flammable liquids stored indoors exceeds the maximum allowable quantities.

Materials which react with water shall not be stored in the same room with flammable liquids. Oxidizers, if in the same room as flammables, shall be stored separately.

STORAGE CABINETS

In patient care areas, the total stored volume of flammable liquids in approved storage cabinets shall not exceed sixty gallons per five thousand square feet.

In all other facilities, the total stored volume of flammable liquids in approved storage cabinets shall not exceed 20 gallons per one hundred square feet with a maximum of 10 gallons per one hundred square feet being Class I liquid, as defined by the North Carolina Fire Code.

All storage cabinets for flammable liquids shall meet NFPA 30 requirements. Not more than 60 gallons of flammable and combustible liquids may be stored in any single storage cabinet.

STORAGE OUTSIDE OF CABINETS

In patient care areas, the total stored volume of flammable liquids outside of approved storage cabinets shall not exceed ten gallons (not in safety cans) plus 25 gallons (in safety cans) per five thousand square feet. Additional quantities of flammable liquids must be stored in a storage cabinet or storage room.

In all other areas, the total capacity of flammable liquids outside of approved storage cabinets shall not exceed five gallons per one hundred square feet.

REFRIGERATOR STORAGE

Class I flammable liquids as defined by the North Carolina Fire Code shall not be stored in

unapproved or residential-type refrigerators. Storage of flammable liquids in well-sealed containers is permissible in listed flammable storage refrigerators labeled to indicate that they are approved for storing flammable liquids. See Supplement C "Storage of Flammable Chemicals in Refrigerators" for additional information.

HANDLING

Use prudent practices to minimize the fire risk and exposures to flammable liquids:

- All sources of ignition (e.g., Bunsen burners, hot plates, open flames, electrical equipment that is not intrinsically safe, etc.) should be eliminated from areas in which flammable materials are used.
- Ensure proper grounding and avoid creating static electricity. Be sure to ground metal containers when transferring flammable liquids.
- Use a chemical fume hood or other local exhaust, where available, to capture vapors when appreciable quantities of flammable substances are being used.
- Keep containers of flammable chemicals closed at all times when not in use.
- Avoid wearing flammable clothing (such as many synthetics).

GASES UNDER PRESSURE

HAZARDS

Gas cylinders have several hazards associated with them: impact from falling, dropping, rolling, or pinching; exposure to hazardous cylinder contents; fire resulting from escape of flammable gas/fluids; and unintentional release of energy from over-pressurization or beheading a valve.

MARKING

All compressed gas cylinders shall be legibly marked by stenciling or stamping with at least the chemical name or commonly accepted name of the material contained. After December 1, 2015, gas cylinders must have a GHS compliant label. In addition, cylinders should bear the approved markings of the Department of Transportation stamped in the metal at the top of the cylinder.

STORAGE AND HANDLING

- Inspect cylinders before use and when delivered. Send back any that are corroded, are not clearly labeled as to contents or cannot be opened with normal force.
- Select the correct regulator for the gas.
- Cylinders (full or empty) shall be appropriately secured by chains, straps, or other sturdy tie downs to prevent falling and rolling during use, storage and transport. They shall be stored and used in an upright position. They shall be transported using a hand truck specifically designed for this purpose.
- Cylinders designed for protective caps must have the caps in place at all times unless the cylinders are in use.
- Cylinders shall be grouped by type of gas and the groups segregated as to compatibility.
- Full cylinders shall be separated from empty cylinders within the storage area.
- Flammable gases shall be separated from nonflammable gases.
- Cylinders shall not be stored at temperatures above 125 °F, in direct sunlight, or outside of the temperature range specified by the manufacturer.
- Cylinders shall be protected against tampering and damage.

- Cylinders shall not be stored near combustible materials. Cylinder valves shall be kept closed when not in use.
- Cylinders shall not be refilled by Duke employees or students.
- Open flames and smoking shall not be permitted in areas where oxygen is used or stored. “Oxygen in Use: No Open Flames” signs shall be posted in these indoor areas. "No Smoking" and "No Open Flames" signs shall be conspicuously posted in these outdoor areas.
- Toxic or highly toxic gases shall be stored in areas containing adequate exhaust ventilation.
- Cylinders, except for those containing compressed air, shall not be used or stored in cold rooms or other unventilated enclosures. An exception may be approved by OESO for inert gases when an oxygen monitor is in place.
- Due to the potential fire hazard, the use of portable containers of liquefied petroleum gases having a water capacity greater than 2½ pounds (Nominal 1 pound LP-Gas capacity) must be approved by the OESO Fire Safety Division.

CRYOGENS

HAZARDS

The following are common hazards associated with cryogens:

Oxygen Deficiency - Liquefied gases, when used in large quantities, may dilute or displace the life sustaining atmosphere. For example, ten liters of liquid nitrogen, upon vaporization, will create a life-threatening environment in a 10 ft by 20 ft by 10 ft room.

Air Freezing (potentially leading to over-pressurization) - Liquid helium and hydrogen are cold enough to solidify atmospheric air. Leaks in the storage systems for these gases may become plugged with solidified air. Particularly affected are pressure relief devices which, if plugged, may cause container over-pressurization and failure.

Oxygen Enrichment - Certain liquefied gases, such as helium, hydrogen, and nitrogen, have the ability to condense oxygen out of the air. As the system is replenished to make up evaporation losses, liquid oxygen will build up as a contaminant. If the system or process is not compatible with liquid oxygen, violent reactions may occur.

Tissue Damage- Severe burns or frostbite can occur upon contact with cryogenic materials.

STORAGE AND HANDLING

Cryogenic fluids should be handled only by persons with adequate understanding of the material, the system in which they are used, and the equipment necessary for safe handling. The following general guidelines shall be adhered to:

- Each part of the cryogenic system must have its own pressure relief system.
- Adequate ventilation must be available in rooms where cryogens are used.
- In areas connected to outdoor cryogen tanks, or where very large quantities of cryogens are stored or used, OESO must be contacted to evaluate the need for additional ventilation and/or oxygen sensors.
- Only Dewars which were designed for the particular cryogen are to be used. Storage containers must be inspected daily to ensure no air or ice plugs exist in the neck openings.
- Hollow rods or tubes must never be used as dipsticks. When a warm tube is inserted into a cryogen, liquid will spout from the top of the tube.

- Liquid levels should be checked regularly. If higher than normal evaporation rates are observed, the Dewar may be losing its vacuum.
- If cryogenic liquids must be transported by elevator, the transport container shall be equipped with a tight fitting cap to prevent leakage. Only containers certified by the manufacturer to have a leakage rate of less than or equal to 1 liter of liquid or 1 kilogram of solid per day shall be used for elevator transport.
- Cryogenic liquids or dry ice storage in walk-in cold rooms is prohibited.
- Use and store liquid hydrogen, helium, and nitrogen away from flammable materials and ignition sources, as these gases can condense oxygen out of the air.
- For liquid helium and hydrogen storage systems, check the pressure relief and inspect the system for leaks regularly. These gases are cold enough to solidify atmospheric air; leaks in storage systems for these gases may become plugged with solidified air. If the pressure relief device becomes plugged, the container may over-pressurize and fail.
- Open flames and smoking shall not be permitted in areas where liquid oxygen is stored or used. “Liquid Oxygen in Use: No Open Flames” signs shall be posted in these indoor areas. "No Smoking" and "No Open Flames" signs shall be conspicuously posted in these outdoor areas.

LABELING

Storage Dewars, process vessels, piping, etc. shall be labeled with the name of the contents. Labels must be protected so they will remain intact and legible. A label must be replaced whenever any portion becomes damaged or illegible.

CORROSIVES

Hazards

Corrosive materials will destroy body tissues. The seriousness of the injury depends on such factors as the type and concentration of the chemical, the body parts contacted, and the rapidity of first aid measures. In general, the hazards are:

Skin contact: Most concentrated acids and bases are corrosive and must be immediately flushed with water. Acids, especially when in concentrated form, are likely to cause immediate pain when they contact the skin; however, strong bases may not cause immediate pain. This may result in a longer contact time and a more serious injury if not flushed immediately.

Eye contact: The eyes are especially susceptible to corrosive liquids, vapors, dusts, or mists and may sustain irreversible damage.

Inhalation: Corrosive vapors, mists, and dusts act on the body in two ways: irritation of the air passages of the nose, throat, and lungs; and absorption of the substance from the lungs into the bloodstream. The severity of the injury will depend on the concentration in air and the duration of the exposure.

Ingestion: Ingestion causes severe burns to the mucous membranes of the mouth, throat, esophagus, and stomach.

Fire or explosions: Concentrated aqueous solutions of inorganic acids are not flammable. Combustion can occur, however, when an acid is mixed with other chemicals or with combustible materials. Acids react with many metals, resulting in a release of flammable hydrogen gas. Some acids, like nitric and percholoric acids, are strong oxidizing agents and

can react violently with organic or other oxidizable materials.

STORAGE AND HANDLING

The corrosive nature of these materials and their ability to produce fires or explosions make the following considerations mandatory in the selection of a storage site:

- A relatively cool, dry environment free from extremes of temperature should be maintained.
- Acids and bases should be stored in a manner that separates them from other materials and from each other. Secondary containment is useful to ensure that if a leak or spill occurs, the material will stay segregated. Each acid or base should be stored in a manner consistent with its properties.
- Small containers (4 L or less) should be placed on material that is acid resistant. Do not store directly on metal shelves unless they have a corrosion-proof coating.
- Carboys should be stored in the same manner as small containers; preferably covered, not stacked, and on acid resistant material.
- All drums should be stored on individual racks or securely blocked with skids with the closure plugs facing up to prevent leakage.
- Do not store corrosives under sinks, as this can lead to corrosion of supply and drain pipes.

When handling:

- Never pour water into acid. Slowly add acid to the water while stirring.
- Never empty carboys or drums of chemicals by means of air pressure. Use a tilting rack, a safety siphon, or a liquid pump.
- Never siphon or pipette by mouth.
- Open bottles or carboys slowly and carefully.
- Flush the outside of the container with water after use to clean off any droplets of material.
- When containers are completely empty, flush thoroughly with water before throwing them away.
- Install an eyewash in all areas where acids and bases are used. A safety shower is necessary where large quantities of corrosive chemicals are used. (See Supplement O “Emergency Eyewash and Shower Equipment”.)
- Never mix acid wastes with other materials such as solvents, metal-containing solutions, etc. Explosive mixtures may be formed.
- Work in areas with adequate ventilation to prevent accumulation of vapors and mists.

HIGHLY TOXIC AND TOXIC MATERIALS; CARCINOGENS; SENSITIZERS; REPRODUCTIVE TOXINS; NANOMATERIALS

HAZARDS

These categories of materials are known to cause various health hazards, some with specific target organ effects.

STORAGE AND HANDLING

- Refer to the appropriate Safety Data Sheet (SDS) for the chemical, physical and toxicological properties of the material to determine appropriate procedures and controls to minimize exposure to individuals.
- Use a chemical fume hood or other local exhaust for work with open volatile toxic liquids. If

aerosols may be produced, toxic powders (and any suspensions of toxic powders) must be handled in a chemical fume hood, exhausted biological safety cabinet with negative pressure ductwork, or other exhausted enclosure. Aerosols may be produced during any open handling of dry powder, and during open or pressurized manipulations of suspensions.
- Work in areas with adequate ventilation to prevent accumulation of vapors and mists.
- Keep containers closed as much as possible.
- Utilize work practices that minimize exposure.
- Transport toxic materials in secondary containment.
- Store away from incompatibles, off of the floor, in tightly sealed containers, and in secondary containment where practicable.

REACTIVE MATERIALS (INCLUDING EXPLOSIVES, ORGANIC PEROXIDES, OXIDIZERS, PYROPHORIC MATERIALS, UNSTABLE MATERIALS, AND WATER REACTIVE MATERIALS)

HAZARDS

These categories of materials are known to cause violent reactions, potentially leading to fire or explosion. Some materials in these categories also create or react to create health hazards.

STORAGE AND HANDLING

It is critical that reactive materials be stored away from incompatibles, off of the floor, in tightly sealed containers, and in unbreakable secondary containment or otherwise indicated by the manufacturer. Refer to the specific Safety Data Sheets (SDS) for storage and compatibility information.

- Store oxidizers away from flammables and combustibles, including wooden shelves, cabinets, and pallets.
- Store and use pyrophoric materials under an inert atmosphere or under kerosene as appropriate. Store pyrophoric materials away from flammables and oxidizers.
- Store organic peroxides where they will not be exposed to air.
- Store water reactives away from sinks and water-based solutions.
- Reactive materials require the presence of a compatible fire extinguisher, as determined in consultation with OESO Fire Safety.
- Doors to rooms storing water reactive materials shall have a warning sign posted.
- Do not allow organic peroxides to evaporate to near dryness. Consult the SDS to determine how long an opened container can be used safely, and dispose of unused amounts after that period of time has passed (or if peroxides are found to be present by testing).
- Use extreme caution when handling and transporting reactives.
- Limit quantities in storage to necessary amounts (as low as practical). Specifically, try to limit amount in storage to what is needed until the next routine order/delivery cycle.
- Avoid working alone with reactive materials.
- When reactive materials are in use, do not leave them unattended.

REFERENCES

Code of Federal Regulations:

Title 29, Part 1910.101 - 111 (OSHA), *Hazardous Materials*

Title 29, Part 1910.1200 (OSHA), *Hazard Communication* (including Appendices)

Title 49, Parts 171 - 179 (DOT), *Hazardous Materials Regulations*

North Carolina State Building Code

National Fire Protection Association:

30, *Flammable Liquids Code*

58, *LP Gas Storage and Use*

59, *LP Gas, Utility Plants*

99, *Health Care Facilities*