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This document is intended to provide an overview of various groups of hazardous chemicals, their characteristics and potential health effects. Refer to the following documents for related information:

[Appendix A - Glossary of Hazardous Materials Hazard Terms.](#)

[Appendix C - Toxicity and Hazard Exposure Assessment](#)

[Appendix D – Handling and Storage of Hazardous Materials](#)

1 Allergens and Sensitizers

An allergic reaction is an adverse immune response following repeat contact with otherwise harmless substance. A chemical allergen is a chemical substance that produces an allergic reaction.

Sensitizers are materials that may cause little or no reaction upon first exposure. Repeated exposures may cause a substantial portion of exposed people to develop an allergic reaction to a chemical substance. A person may be exposed to an allergen by inhalation, ingestion, or penetration of the skin. The reaction may be as mild as a rash (contact dermatitis) or as serious as anaphylactic shock. Reactions can be delayed, taking hours or even days to develop. The skin is usually the site of such delayed reactions, becoming red, swollen and itchy. A delayed reaction can even occur sometime after the chemical has been removed.

Once sensitized, repeated exposures to even the most minute levels of sensitizers can result in life-threatening allergic reactions. Allergens and sensitizers include a variety of substances capable of producing skin and lung hypersensitivity.

Examples of common substances include: epoxides, nickel compounds, poison ivy, toluene diisocyanate and other isocyanates, chlorinated hydrocarbons, chromium compounds (i.e., chromates), formaldehyde, amines, beryllium compounds, diazomethane, latex and certain phenols.

NOTE: Some people who often use latex-containing products may develop sensitivity to the latex. A sensitized individual's reaction to latex exposure can eventually include anaphylactic shock, which can result in death. To minimize exposure to latex, use non-latex containing gloves, such as nitrile gloves.

2 Anesthetics

Anesthetics are materials that depress the central nervous system, particularly the brain, producing loss of sensation or feeling. Examples include: diethyl ether, alcohols and halogenated hydrocarbons (chloroform, trichloroethylene, carbon tetrachloride).

3 Asphyxiates

Asphyxiants are substances that interfere with the transport of oxygen either in the lungs or in the red blood cells, depriving tissues and organs of oxygen. The brain is the system most easily affected by lack of oxygen and exposure to asphyxiants can be deadly.

- Simple asphyxiants are inert gases that displace oxygen in the air and include such substances as: nitrogen, carbon dioxide, helium, nitrous oxide and argon. Under certain conditions, even chemically inert and benign substances may be dangerous.
- Chemical asphyxiants combine with hemoglobin and render the body incapable of using an adequate oxygen supply. These chemical asphyxiants are toxic even at

very low concentrations (e.g., a few ppm) in air and include substances such as carbon monoxide, hydrogen cyanide, and hydrogen

4 Biological Hazards

Biological hazard (biohazard) refers to plants, animals, or their products that may present a potential risk to the health and well-being of humans or animals and the environment. Infectious biological agents can be bacterial, viral, rickettsia, fungal, or parasitic. This also includes items such as human body fluids or tissue (e.g. blood, urine, saliva, etc.) which have the potential to be carry blood borne pathogens.

5 Carcinogens

A carcinogen is any substance that contains an agent that can initiate or speed the development of malignant or potentially malignant neoplastic proliferations of cells (i.e., causes cancer). Many chemicals have been evaluated for their ability to cause cancer. It is believed that these carcinogens directly or indirectly interact with cellular DNA causing permanent alterations. Carcinogens are chronically toxic substances because they cause damage after repeated or long-duration exposure and the effects may not become evident for many years after exposure has stopped. The latent period, the length of time from exposure to cancer formation, for many cancers ranges from twenty to forty or more years. The risk of developing cancer from exposure to a chemical increase with the length of exposure and with the chemical's exposure concentration.



There is a distinction between *human carcinogens* and *suspected human carcinogens*. The term human carcinogen is used when there is clear evidence of a chemical's ability to cause cancer in humans. Suspected human carcinogen refers to chemicals that have been shown to cause cancer in two or more animal species and are therefore suspected of also causing cancer in humans. Examples of known carcinogens include: asbestos, benzene, tobacco smoke, hexavalent chromium, aflatoxins.

Zero exposure should be the goal when working with known or suspected carcinogens. Persons working with or planning to work with carcinogens or suspected carcinogens must follow strict guidelines to minimize exposure. For a specific substance, the Toxicity Data section of the SDS will state whether the substance is considered a carcinogen by OSHA, the National Toxicology Program (NTP), or the International Agency for Research on Cancer (IARC).

Chemical Carcinogens Regulated by OSHA

	Citation		Citation
2-Acetylaminofluorene	1910.1014	4-Dimethylaminoazobenzene	1910.1015
Acrylonitrile	1910.1045	Ethyleneimine	1910.1012
4-Aminodiphenyl	1910.1011	Ethylene oxide	1910.1047
Arsenic, inorganic	1910.1018	Formaldehyde	1910.1048
Asbestos	1910.1001	Methyl chloromethyl ether	1910.1006
Benzene	1910.1028	Methylene chloride	1910.1052
Benzidine	1910.1010	Methylenedianiline	1910.1050
1,3-Butadiene	1910.1051	a-Naphthylamine	1910.1004

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bis-Chloromethyl ether	1910.1008	b-Naphthylamine	1910.1009
Cadmium	1910.1027	4-Nitrobiphenyl	1910.1003
Chromium (VI)	1910.1026	N-Nitrosodimethylamine	1910.1016
Coke oven emissions	1910.1029	b-Propiolactone	1910.1013
1,2-Dibromo-3-chloropropane	1910.1044	Vinyl chloride	1910.1017
3,3'-Dichlorobenzidine (and its salts)	1910.1007		

[29 CFR 1910 Subpart Z](#)

This list of carcinogens is only one of many available lists of confirmed and suspected human carcinogens.

Lists of carcinogens published by the following agencies and organizations:

[American Conference of Governmental Industrial Hygienists \(ACGIH\)](#)

[International Agency for Research on Cancer \(IARC\)](#)

[National Institutes of Occupational Safety and Health \(NIOSH\)](#)

[National Toxicology Program \(NTP\)](#)

6 Compressed gas

A compressed gas is any material which at room temperature and atmospheric pressure is a gas, but is contained under pressure as a compressed, liquefied or dissolved gas. Compressed gases present a physical hazard due to the storage pressure, but can also exhibit overt hazards such as, flammability, corrosivity, or toxicity. Examples: hydrogen (compressed gas), acetylene (gas dissolved in a solvent) and chlorine (liquefied gas).



If compressed gases are accidentally released, they may cause the following:

- Depleted oxygen atmosphere, potentially resulting in asphyxiation (includes inert gases)
- Fire or explosion
- Adverse health effects from chemical exposure
- Physical damage to facilities or injuries to personnel because of the sudden release of potential energy

IMPORTANT: Cylinders can travel through walls much like a torpedo travels through water. They can cause structural damage, severe injury, and even death.

Because disposal of compressed gas cylinders is difficult and expensive, be sure to arrange a return agreement with suppliers prior to purchase.

Some gases (e.g., arsine, phosphine, phosgene, nitric oxide, chlorine, sulfur tetrafluoride, etc.), are potentially lethal if the cylinder leaks and the leakage of a flammable gas can create an explosive atmosphere. In a laboratory fire, the heat may cause the cylinder's internal pressure to increase and the cylinder may rupture.

Cylinders that are knocked over or dropped can also be very dangerous and can cause serious injuries. A cylinder may contain a gas at a maximum pressure of 150 atmospheres. If all the gas were released from a 50 kg cylinder through the 2-cm diameter opening, the

cylinder could be launched at a velocity of about 75 mph. Thus, a broken cylinder valve may cause the cylinder to act like a missile, passing through walls and possibly causing structural damage, severe injury, and death.

7 Corrosives

A corrosive is a chemical that can cause visible destruction of or irreversible alterations in living tissue by chemical action at the site of contact. Corrosives can also react (e.g., oxidation) with metals causing deterioration of the metal surface. Acids and bases are corrosives. Aqueous solutions of acids with a pH less than 2, and bases with a pH greater than 12 are especially dangerous and require special precautions.



Examples of common corrosives are:

- | | | |
|-------------------------------|--------------------------|-----------------------|
| acidic corrosives: | • hydrochloric acid | • sulfuric acid |
| alkaline corrosives: | • sodium hydroxide (lye) | • potassium hydroxide |
| corrosive dehydrating agents: | • phosphorous pentoxide | • calcium oxide |
| corrosive oxidizing agents: | • chromic acid | • perchloric acid |
| organic corrosives: | • phenol | • acetic acid |

Because chemical corrosion covers a broad range of reactions that degrade structural materials, when working with chemicals, you must understand the reactions that are possible. Common reactions include: rusting steel, thinning glass-walled containers, softening hard plastic, disintegrating fabrics and living tissue cell destruction. These reactions can result from different types of chemical attacks: oxygen in moist air, aqueous hydrofluoric acid, solvents on plastics, acids on cellulose, bases on wool or leather, and a variety of lipid soluble chemicals on tissue. Some common material reactions include:

- Non-polar volatile liquids (e.g., alkylphosphines, amines and chlorinated solvents) can affect the structural integrity of containers and stoppers by being absorbed into rubber stoppers, septums and plastic containers causing swelling, softening or embrittlement.
- Ground glass stoppers can be frozen in due to welding of glass by action of dilute hydroxide from strong or weak bases and by fluoride ion, as acid or salt.
- Ethylene glycol, more so than any alcohol, has an enhanced tendency to promote rusting of the iron of its steel container (e.g., drum or five gallon can).

While pH describes the hydrogen ion concentration, it is not an absolute measurement of potential hazard. Sometimes, weak acids at high concentration can be more destructive to tissue than strong acids at lower concentrations. For example, 13 M acetic acid (i.e., 1:1 Cl-13CO₂H-H₂O) with a pH of 1.25 (0.42% dissociated) is a greater danger to skin than sulfuric acid at the same pH (i.e., 0.056 M) because it is more able to penetrate skin. Hydroxide ion at pH 13 is a greater danger to skin than aqueous strong acid at pH 1 because proteins and lipids are more sensitive to bases. Phenol is not a strong acid but will readily penetrate skin and cause destruction by coagulation of proteins in cells and then enter the blood capillaries.

7.1 Health Consequences

Extreme caution should be taken when handling corrosive chemicals, or severe injury may result.

- a. Concentrated acids can cause painful and sometimes severe burns.
- b. Inorganic hydroxides can cause serious damage to skin tissues because a protective protein layer does not form. Even a dilute solution such as sodium or potassium hydroxide can saponify fat and attack skin.
- c. At first, skin contact with phenol may not be painful, but the exposed area may turn white due to the severe burn. Systemic poisoning may also result from dermal exposure.
- d. Skin contact with low concentrations of hydrofluoric acid (HF) may not cause pain immediately but can still cause tissue damage if not treated properly. Higher concentrations of HF (50% or greater) can cause immediate, painful damage to tissues.

7.2 Special Precautions for Hydrogen Fluoride / Hydrofluoric Acid

Hydrogen Fluoride is a colorless fuming gas or liquid. In its liquid state it's called Hydrofluoric Acid (HF). HF is an extremely corrosive material. All forms, including vapors and solutions, can cause severe, slow-healing burns to human tissue, including the lungs and eyes. At concentrations greater than 50% the burning is noticeable in a matter of minutes or less, while at concentrations below 50% the burns may not be felt until several hours after exposure. Burns from concentrated acid involving as little as 2.5% of body surface have resulted in death. Because it has a low boiling point and a high vapor pressure, HF must be kept in a non-glass pressure container. HF dissolves glass; therefore, it should never be stored in a glass container.

IMPORTANT: If you are exposed to HF gas, seek immediate care at the nearest hospital emergency room. For contact with HF acid, flush with large amounts of cold water for at least 15 minutes while removing contaminated clothing. Apply calcium gluconate gels and seek immediate emergency medical attention.

8 Cryogenic Materials

A cryogenic material is normally a gas at room temperature but that has been cooled to a temperature where it condenses to a liquid. Most cryogenic liquids are odorless, colorless, and tasteless. Cryogenic liquids are hazardous because of the physical hazard due to their extremely cold temperatures (less than -150oC). and the chemical characteristics of their super-cooled state.

Cryogenic fluids are extremely cold liquefied gases, such as liquid nitrogen or liquid oxygen, and are used to obtain extremely cold temperatures. When cryogenic liquids are exposed to the atmosphere, however, they create a highly visible and dense fog.

Cryogenics pose numerous hazards. A person who is exposed to cryogenics can have significant health consequences. All cryogenics, apart from oxygen, can displace breathable air and can cause asphyxiation. Cryogenics can also cause frostbite on exposed skin and eye tissue.

IMPORTANT: Be aware of the tremendous expansion and threat of asphyxiation when a cryogenic liquid vaporizes at room temperature.

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There is also an increased risk of fire in areas where liquid cryogenics are stored and used. For example, cryogenic vapors from liquid oxygen, liquid hydrogen or other flammable cryogenics may cause a fire or explosion if ignited. Materials that are normally noncombustible (e.g., carbon steel) may ignite if coated with an oxygen-rich condensate. Liquefied inert gases, such as liquid nitrogen or liquid helium, are capable of condensing atmospheric oxygen and causing oxygen entrapment or enrichment in unsuspected areas. Extremely cold metal surfaces are also capable of entrapping atmospheric oxygen.

The gases in a solution of liquefied gases (e.g., liquid air) may evaporate at different rates leaving a concentration of a flammable gas. A cryogenic liquid spill (e.g., liquid nitrogen) on a person could be injurious almost immediately and it could be made worse by being spilled onto clothing that could trap larger amounts of cold liquid than would contact the otherwise unprotected skin. Because pressures may build up rapidly in a closed system, adequate venting is required.

Because the low temperatures of cryogenic liquids may affect physical properties of materials such as stainless steel or aluminum, take care to select equipment materials accordingly.

Cryogenic Hazard Source	Hazard
Hydrogen, methane, acetylene	Gases are flammable
Oxygen	Increases the flammability of combustibles
Liquefied inert gases	Air oxygen condensation and concentration
Extremely cold surfaces	Materials made brittle

Liquefied gas is more concentrated than its vapor and may rapidly evaporate. Liquid nitrogen experiences a 700-fold increase in volume going from the condensed phase to the vapor phase. Five gallons could displace half the air in a 15' x 15 room, leaving only 10% oxygen (e.g., like the top of the Himalayas).

9 Environmental Toxins

Some chemicals are or may be very toxic to wildlife or can otherwise harm ecosystems but pose less risk to humans. Some factors contributing to environmental toxicity are persistency (resistance to degradation) and bioaccumulation as the chemical moves up the food chain. For some environmental toxins the degree of human toxicity is uncertain or controversial. DDT and polychlorinated biphenyls (PCBs) are examples of chemicals that have been shown to cause reproductive failure in certain species but appear to be less hazardous to humans. Despite these species' differences, careful use and disposal of environmental toxins is required.



10 Flammable and Combustible Liquids

The DOT defines a combustible liquid as a liquid with a flash point above 141°F and below 200°F. NFPA and OSHA define it as a liquid with a flash point at or above 100°F but below 200°F. These liquids, even though not classified as flammable liquids, still present a significant fire hazard. Examples: kerosene, glacial acetic acid and phenol.



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Flammability is the tendency of a chemical to burn. Flammable and combustible chemicals are those chemicals that evaporate rapidly and generate enough vapor to ignite in the presence of an ignition source (i.e., catches fire easily and burns readily). Flammable substances can be solid, liquid, or gaseous, but the most common type encountered in a laboratory setting is a flammable liquid or the vapor produced from such a liquid. Flammable chemicals are classified according to their flash point, boiling point and ignition temperature.

- Flash point (FP) is the lowest temperature at which a flammable liquid gives off enough vapor to ignite.
- Boiling point (BP) is the temperature at which the vapor pressure of a liquid is equal to the atmospheric pressure under which the liquid vaporizes. Flammable liquids with low boiling points generally present special fire hazards.
- Ignition (or auto-ignition) temperature is the lowest temperature at which a chemical will ignite and burn independently of its heat source. The lower the ignition temperature, the greater the fire potential. When the flammable vapor reaches its auto-ignition temperature, a spark is not needed for ignition

Additionally, flammable and combustible chemicals are those that can react with oxidizers to cause a fire or explosion (i.e., a compound may burn so rapidly that it produces an explosion). Combustible materials will generate enough vapors at or above 38 °C (100 °F). Flammable chemicals will generate enough vapors at temperatures below 38 °C (100 °F). The table illustrates flammable and combustible class characteristics per NFPA.

	Flammable			Combustible	
	I-A	I-B	I-C	II	III
Flash Point	< 23 °C (73 °F)	< 23 °C (73 °F)	≥ 23°C (73 °F) < 38 °C (100°F)	≥38°C <60°C (100°F) (140°F)	≥60°C(140°F) <93°C (200°F)
Boiling Point	<38 °C (100 °F)	≥ 38 °C (100 °F)	---	---	---

Different agencies use different temperatures to define flammable liquids:

DOT ≤ 60 °C ≤ (141 °F) EPA < 60 °C < (140 °F) (ignitable) NFPA ≤ 37.8 °C ≤ (100°F)

For laboratory use and storage purposes we utilize the NFPA definitions.

Flammable and combustible chemicals are also characterized by their explosive limits. The lower explosive limit (LEL) or lower flammable limit is the lowest vapor concentration of the substance that will produce a flash of fire (i.e., blast) when an ignition source is present. The upper explosive limit (UEL) or upper flammable limit is the highest vapor concentration of the substance that will produce a flash of fire when an ignition source is present. A substance's flammable range consists of all concentrations between the LEL and the UEL. The range may be dependent upon temperature and oxygen concentration. At higher concentrations than the UEL, the mixture is too rich to burn and at concentrations lower than the LEL, the mixture is too lean to burn. Note that, for flammable chemicals that are also toxic, concentrations at which the flammability is a hazard are usually well above the toxicity hazard concentrations.

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The flammable liquids of most concern in laboratories are those that have flash points below room temperature, about 27 °C (80.6 °F). Flash points and flammability classifications of a few common laboratory liquids are:

Substance	°C	°F	Class	Substance	°C	°F	Class
Acetaldehyde	- 39	- 38	I-A	Gasoline	- 46	- 50	I-A
Acetone	-18	0	I-B	Glacial acetic acid	40	104	II
Benzene	-11	12	I-B	Heptane	-4	25	I-B
Carbon disulfide	- 29	-20	I-B	Hexane	-18	0	1-B
Cyclohexane	-17	1	I-B	Methanol	12	54	I-B
Cyclohexanol	68	154	III	Pentane	- 40	- 40	1-A
Ethanol	13	55	I-B	Petroleum ether	- 40	- 40	1-A
Ethyl acetate	- 4	24	1-B	Styrene monomer	32	90	1-C
Ethyl chloride	- 50	- 58	I-A	Toluene	4	40	I-B
Ethyl ether	- 45	- 49	I-A	Xylene	29	84	1-C

Thus, xylene, with a flash point of 29 °C, or just above room temperature, is often used as a less toxic and safer substitute for benzene, with a flash point of -11 °C.

Organic solvents are often the most hazardous chemicals in the work place. Solvents such as ether, alcohols, and toluene, for example, are highly volatile and flammable. Perchlorinated solvents, such as carbon tetrachloride (CCl₄), are non-flammable. But most hydrogen-containing chlorinated solvents, such as chloroform, are flammable. When exposed to heat or flame, chlorinated solvents may produce carbon monoxide, chlorine, phosgene, or other highly toxic gases.

Always use volatile and flammable solvents in an area with good ventilation or preferably in a fume hood. Never use ether or other highly flammable solvents in a room with open flames or other ignition sources present, including non-intrinsically safe fixtures. Remember, chemical flames of hydrogen and methanol are invisible, the vapors of flammable chemicals are invisible and a vapor trail to an ignition source can result in a flashback. However, for a fire to occur three conditions must occur simultaneously and in close proximity:

- an oxidizing atmosphere (e.g., air)
- a concentration of a flammable gas or vapor
- an ignition sources.

The key to reducing fire risk is to control one or more of these three factors. Control the ignition source first, vapor production second, and oxygen third

Health hazards associated with solvents include exposure by the following routes:

- Inhalation of a solvent may cause bronchial irritation, dizziness, central nervous system depression, nausea, headache, coma, or death. Prolonged exposure to excessive concentrations of solvent vapors may cause liver or kidney damage. The consumption of alcoholic beverages can enhance these effects.
- Skin contact with solvents may lead to defatting, drying, and skin irritation

- Ingestion of a solvent may cause severe toxicological effects. Seek medical attention immediately.

The odor threshold for the following chemicals exceeds acceptable exposure limits. Therefore, if you can smell it, you may be overexposed — increase ventilation immediately! Examples of such solvents are:

- Chloroform
- Benzene
- Carbon tetrachloride
- Methylene chloride

NOTE: Do not depend on your sense of smell alone to know when hazardous vapors are present. The odor of some chemicals is so strong that they can be detected at levels far below hazardous concentrations (e.g., xylene).

Some solvents (e.g., benzene) are known or suspected carcinogens.

To decrease the effects of solvent exposure, substitute hazardous solvents with less toxic or hazardous solvents whenever possible. For example, use hexane instead of diethyl ether, benzene or a chlorinated solvent.

11 Irritants

Irritants are materials that cause a reversible inflammation or irritation to the eyes, respiratory tract, skin, and mucous membranes. The inflammation occurs at concentrations far below those needed to cause tissue destruction. Chronic exposure to irritants can cause increased mucous secretions and result in chronic bronchitis. Commonly encountered irritants include:

- ammonia
- hydrogen chloride
- halogens (F₂, Cl₂, I₂)
- phosgene
- nitrogen dioxide
- arsenic trichloride
- hydrogen fluoride
- ozone
- diethyl/dimethyl sulfate
- phosphorus chlorides
- alkaline dusts and mists (hydroxides, carbonates, etc.)

Irritants that can also produce chemical asthma by causing changes in the mechanics of respiration and lung function include:

- sulfur dioxide
- sulfuric acid mist
- acetic acid
- acrolein
- iodine vapor
- formaldehyde
- formic acid

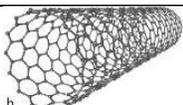
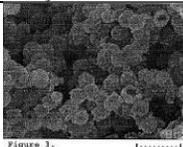
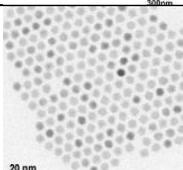
A primary irritant (e.g., hydrogen chloride) exerts no systemic toxic action because the products formed on the tissue of the respiratory tract are nontoxic or because the irritant action is far in excess of any systemic toxic action. A secondary irritant's effect on mucous membranes is overshadowed by a systemic effect resulting from absorption. Examples of secondary irritants include hydrogen sulfide and aromatic hydrocarbons. Exposure to a secondary irritant can result in pulmonary edema, hemorrhage and tissue necrosis.

12 Nanomaterials

Nanotechnology is an emerging industry and area of research that involves the engineering of items on a molecular level. Considerable advancements in nanotechnology have already been made and this is a growing area of research at UCCS. Because of the broad range of possible nanotechnology applications, continued evaluation of the potential health risks associated with exposure to nanomaterial (NM) is essential to ensure their safe handling.

Engineered nanoparticles are materials purposefully produced with at least one dimension between 1 and 100 nanometers. Nanomaterials are both naturally occurring in the environment and intentionally produced. Intentionally produced nanomaterials are referred to as Engineered Nanomaterials (ENMs). Nanoparticles (NPs) often exhibit unique physical and chemical properties that impart specific characteristics essential in making engineered materials, but little is known about what effect these properties may have on human health. Research has shown that the physicochemical characteristics of particles can influence their effects in biological systems. These characteristics include particle size, shape, surface area, charge, chemical properties, solubility, oxidant generation potential, and degree of agglomeration. Until the results from research studies can fully elucidate the characteristics of NPs that may pose a health risk, precautionary measures are warranted. The most common types of ENMs are carbon-based materials such as nanotubes, metals and metal oxides such as silver and zinc oxide, and quantum dots made of compounds such as zinc selenide

Types of Nanomaterials

	Type	Examples
	Carbon Based	Buckyballs or Fullerenes, Carbon Nanotubes#, Dendrimers <i>Often includes functional groups like * PEG (polyethylene glycol, Pyrrolidine, N,N-dimethylethylenediamine, imidazole</i>
	Metals and Metal Oxides	Titanium Dioxide (Titania)**, Zinc Oxide, Cerium Oxide (Cerial), Aluminum oxide, Iron Oxide, Silver, Gold, and Zero Valent Iron (ZVI) nanoparticles
	Quantum Dots	ZnSe, ZnS, ZnTe, CdS, CdTe, CdSe, GaAs, AlGaAs, PbS, InP <i>Includes crystalline nanoparticle that exhibits size-dependent properties due to quantum confinement effects on the electronic states (ISO/TS 27687:2008)</i>

* Carbon Nanotubes are subject to a proposed Recommended Exposure Limit of TWA 7 ug/m³ due to the risk of developing respiratory health effects.

** Nano-Titanium Dioxide is subject to a proposed Permissible Exposure Limit of TWA 0.3 mg/m³ due to the risk of developing lung cancer. There are mixed studies regarding TiO₂ skin penetration. Some

studies indicate TiO₂ and ZnO does not pass through the stratum corneum, while others indicate significant penetration through the skin.

12.1 Potential Health Concerns

- The potential for NM to enter the body is among several factors that scientists examine in determining whether such materials may pose an occupational health hazard.
- In general, the risk of exposure is lowest when nanomaterials are bound in a solid matrix with little potential to create airborne dust or when in a non-volatile liquid suspension. The risk of exposure increases when nanomaterials are used as fine powders or are suspended in volatile solvents or gases. Refer to the chart below for risk levels.
- NM has the greatest potential to enter the body through the respiratory system if they are airborne and in the form of respirable-sized particles (NPs). They may also come into contact with the skin or be ingested.
- Based on results from human and animal studies, airborne NPs can be inhaled and deposit in the respiratory tract; and based on animal studies, NPs can enter the blood stream, and translocate to other organs.
- Experimental studies in rats have shown that equivalent mass doses of insoluble incidental NPs are more potent than large particles of similar composition in causing pulmonary inflammation and lung tumors. Results from in vitro cell culture studies with similar materials are generally supportive of the biological responses observed in animals.
- Experimental studies in animals, cell cultures, and cell-free systems have shown that changes in the chemical composition, crystal structure, and size of particles can influence their oxidant generation properties and cytotoxicity.
- Studies in workers exposed to aerosols of some manufactured or incidental microscopic (fine) and nanoscale (ultrafine) particles have reported adverse lung effects including lung function decrements and obstructive and fibrotic lung diseases. The implications of these studies to engineered NPs, which may have different particle properties, are uncertain.
- Research is needed to determine the key physical and chemical characteristics of NPs that determine their hazard potential.
- Although insufficient information exists to predict the fire and explosion risk associated with powders of NMs, nanoscale combustible material could present a higher risk than coarser material with a similar mass concentration given its increased particle surface area and potentially unique properties due to the nanoscale.
- Some NMs may initiate catalytic reactions depending on their composition and structure that would not otherwise be anticipated based on their chemical composition.

12.2 Working with Engineered Nanomaterials

(Adopted from guidelines as written by Dr. Peter Lichty of Lawrence Berkeley National Laboratory and Guidance from NIOSH).

Nanomaterial-enabled products such as nanocomposites, surface-coated materials, and materials comprised of nanostructures, such as integrated circuits, are unlikely to pose a risk of exposure during their handling and use as materials of non-inhalable size. However, some of the processes used in their production (e.g., formulating and applying nanoscale

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coatings) may lead to exposure to NMs, and the cutting or grinding of such products could release respirable-sized nanoparticles.

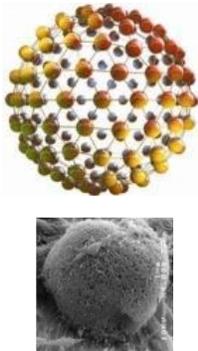
Maintenance on production systems (including cleaning and disposal of materials from dust collection systems) is likely to result in exposure to nanoparticles if deposited NMs are disturbed.

The following workplace tasks can increase the risk of exposure to nanoparticles:

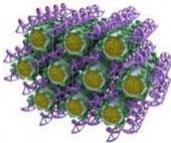
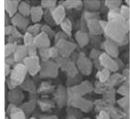
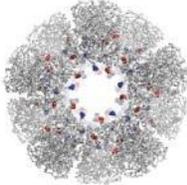
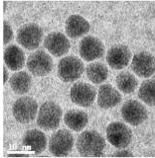
- Working with NMs in liquid media without adequate protection (e.g., gloves)
- Working with NMs in liquid during pouring or mixing operations, or where a high degree of agitation is involved
- Generating nanoparticles in non-enclosed systems
- Handling (e.g., weighing, blending, spraying) powders of NMs
- Maintenance on equipment and processes used to produce or fabricate NMs and the cleaning-up of spills and waste material containing NMs
- Cleaning of dust collection systems used to capture nanoparticles
- Machining, sanding, drilling, or other mechanical disruptions of materials containing nanoparticles

Reason for concern related to potential EHS risks associated with nanotechnologies and in particular, carbon nanotubes, have recently surfaced. For this reason, UCCS's EHS department is recommending an approach referred to as control banding to address the potential risks associated with research in areas concerned with nanotechnologies. Control banding (CB) is a strategy for qualitative risk assessment and management of hazards in the workplace. The strategy involves a process to group workplace risks into control bands based on combinations of hazard and exposure information. CB strategies are not intended to be predictive exposure models. The tables below provide general guidelines for specific nanotechnologies already in use in many areas of research. It is recommended that this table be used a guideline to develop SOP for all nanotechnology related research. At a minimum, any new research involving nanotechnologies should be reviewed from a Process Hazard Analysis perspective.

Control Bands for Nanomaterials

Risk Level	Material State or Type of Use	Examples	
Category 1 Lower Exposure Potential	<p>Material State <i>No potential for airborne release (when handling)</i></p> <ul style="list-style-type: none"> • Solid: Bound in a substrate or matrix • Liquid: Water-based liquid suspensions or gels • Gas: No potential for release into air (when handling) <p>Type of Use</p> <ul style="list-style-type: none"> • No thermal or mechanical stress 	<ul style="list-style-type: none"> • Non- destructive handling of solid engineered nanoparticle composites or nanoparticles permanently bonded to a substrate 	

CLASSIFICATION OF HAZARDOUS MATERIALS

<p>Category 2 Moderate Exposure Potential</p>	<p>Material State <i>Moderate potential for airborne release (when handling)</i></p> <ul style="list-style-type: none"> • Solid: Powders or Pellets • Liquid: Solvent-based liquid suspensions or gels • Air: Potential for release into air (when handling) <p>Type of Use</p> <ul style="list-style-type: none"> • Thermal or mechanical stress induced 	<ul style="list-style-type: none"> • Pouring, heating, or mixing liquid suspensions (e.g., stirring or pipetting), or operations with high degree of agitation involved (e.g., sonication) • Weighing or transferring powders or pellets • Changing bedding out of laboratory animal cages 	 
<p>Category 3 Higher Exposure Potential</p>	<p>Material State <i>High potential for airborne release (when handling)</i></p> <ul style="list-style-type: none"> • Solid: Powders or Pellets with extreme potential for release into air • Gas: Suspended in gas 	<ul style="list-style-type: none"> • Generating or manipulating nanomaterials in gas phase or in aerosol form • Furnace operations • Cleaning reactors • Changing filter elements • Cleaning dust collection systems used to capture nanomaterials • High speed abrading / grinding nanocomposite materials 	 

The following present some scenarios along with control bands for common materials and activities:

<p style="text-align: center;">Green – NSL 1 Nanomaterials consist of Little to no harm - known to be inert</p>	
Scenario Description	Name or Description of Nanomaterial
Gold nanoparticles used to test carbon nanotube filter	Gold nanoparticles
Mixed polystyrene spheres with buffer, etching nanostructures onto semiconductors	Polystyrene spheres, nanostructures
Deposition of liquid-suspended nanoparticles onto surfaces using low voltage electric fields	Polymer latex, gold, platinum, palladium nanoparticles

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Preparation of examples. Activities include cutting, slicing, grinding, lapping, polishing, chemical etching, electrochemical polishing and ion etching	Carbon black, Aluminum (Al) oxide, Mg oxide, polycrystalline diamond suspension, colloidal silica, Palladium (Pd) powder, carbon nanotubes
Sample preparation and characterization	Gold, silver nanoparticle, Iron oxide, silicon dioxide, aluminum oxide, carbon, ceramic
Synthesis of aerogel	Silica, iron, chromium, copper, zinc nanoparticles, titanium nanoparticles
Required: Engineering Controls	General Ventilation
Required: Personal Protective Equipment	Lab coat, safety glasses/goggles single nitrile gloves

Yellow – NSL 2 Nanomaterials consist of Potential Hazards(s)	
SCENARIO DESCRIPTION	NAME OR DESCRIPTION OF NANOMATERIAL
Synthesis of metal oxide nanowires on substrates within a tube furnace	Zinc oxide (ZnO), Tin Oxide (SnO ₂), Titanium Oxide (TiO ₂), Lead zirconium titanium oxide (PBZrTiO ₃), Barium Titanium oxide (BaTiO ₃) and Strontium Titanium oxide (SrTiO ₃) nanowires
Synthesis of silver and copper oxide nanoparticles	Silver (Ag) oxide nanoparticles, Copper (Cu) oxide nanoparticles
Addition of quantum dots onto porous glass	Cadmium selenide, lead sulfide
Growth of palladium nanocatalyst	Palladium nanocatalyst
Water is poured into container with liquid-suspended carbon nanotubes	Carbon nanotubes
Analysis of nanomaterial waste samples in to laboratory	Various
Purification and functionalization of carbon nanotubes	Carbon nanotubes
Synthesis and optical characterization of nanoparticles	Cadmium Selenium (CdSe) quantum dots, germanium quantum dots, iron oxide, gold, lead sulfide nanoparticles
Sample preparation and characterization of CdSe Nanodots	Cadmium Selenium (CdSe) quantum dots
Sample preparation and characterization of carbon diamondoids	Carbon diamondoids
Sample preparation and characterization using laser microscopy	Gold, silver nanoparticles

CLASSIFICATION OF HAZARDOUS MATERIALS

SCENARIO DESCRIPTION	NAME OR DESCRIPTION OF NANOMATERIAL
Preparation of nanofoams sample for microscopy	Gold, copper, aluminum, nickel nanoparticles
Preparation of carbon nanotubes sample for microscopy	Carbon nanotubes
Machining (e.g., turning, milling) of aerogels and nanofoams for target assembly	Silica aerogels, tantulum aerogels, metal nanofoams (copper, gold), carbon nanofoams
Site wide waste sampling activities	Various
Waste accumulation area activities, including waste management, waste packaging, etc.	Various
Radioactive and Hazardous Waste Management field tech activities, including waste management, waste packaging, waste sampling, etc.	Various
Required: Engineering Controls	Fume hood or BSL
Required: Personal Protective Equipment	Lab coat, safety glasses/goggles, single nitrile gloves

Orange – NSL 3	
Nanomaterials – limited information is known	
SCENARIO DESCRIPTION	NAME OF DESCRIPTION OF NANOMATERIAL
Activities related to operating and maintaining a vertical tube quench furnace and horizontal tube furnace	Gold, (Ag) Copper (Cu) Nickel (Ni) brass, Silver (Au) and Platinum (PT) nanoparticles
Required: Engineering Controls	Glove box, fume hood with HEPA or hard ducted BSC
Required: Personal Protective Equipment	Lab coat, safety glasses/goggles, double nitrile gloves

RED – NSL 4	
Nanomaterials information is unknown	
Inhalation hazard	
SCENARIO DESCRIPTION	NAME OF DESCRIPTION OF NANOMATERIAL
Nanomaterial is attached to a chemical that is carcinogenic, etc.	

Required: Engineering Controls	Glove box, fume hood with HEPA or hard ducted BSC
Required: Personal Protective Equipment	Lab coat, safety glasses/goggles double nitrile gloves and N95/N100 respirator

13 Oxidizers

An oxidizer is a material that yields oxygen readily to cause or enhance the combustion (oxidation) of organic matter. Materials that do not contain oxygen can also be oxidizers because of their ability to accept electrons. Examples: nitrates, permanganates, dichromates, peroxides, nitric acid, perchloric acid and chlorine



14 Radiological

Radioactivity is defined as the spontaneous emission of energy over time, generally in the form of particles or light waves, from an atom which is unstable due to an imbalance of neutrons and protons. Radiation may occur as particles (such as alpha particles, beta particles or neutrons) or photons (such as gamma rays or x-rays) emitted from an unstable atom as the result of radioactive decay. Each type of radiation emission has unique safety considerations and handling techniques. Not all forms of radiation produce the same biological effect when they interact with human tissue.

Isotopes are atoms which have the same number of protons and electrons but a different number of neutrons. Therefore, isotopes have different physical properties. Some elements have many isotopes but not all are unstable enough to be radioactive. Isotopes which emit radiation are referred to as radioisotopes.



Each radioisotope emits radioactive energy at a specific rate, which can be measured. The amount of time it takes for half of the atoms in a radioactive sample to emit energy (or decay) is referred to as the half-life of the radioisotope. Half-life becomes very important when choosing a radioisotope to use in a research experiment. Ideally, a researcher will want the radiation to be detectable from a sample long enough to be detected during the experiment, but not so long after that the waste materials are difficult to dispose

15 Reactives

A chemical is reactive, or unstable, if it has a tendency to undergo chemical reaction either by itself or with other materials with the release of energy. Undesirable effects such as pressure build-up, temperature increase or the formation of noxious, toxic or corrosive byproducts may occur because of the chemical's reactivity to heating, shock, direct contact with other materials or other conditions in use or in storage. Reactives can be divided into the following hazard groups:

- Explosives
- Monomers
- Organic Peroxide
- Pyrophoric

- Water Reactives

Any chemical, except for helium and neon, can react with something (e.g., fluorine or platinum hexafluoride). Chemicals that readily react with ordinary unreactive chemicals such as air, water, cellulose, protein and steel, especially if the reaction is vigorous, are called reactive. We also need to distinguish between reactivity and stability. In the above reactive examples, fluorine is stable by itself, but platinum hexafluoride is not; it decomposes to its tetrafluoride and fluorine.

Oxidation is a form of reaction. Some chemicals, called self-reactive, even undergo change without any chemical input. Self-reactivity can have three forms of change; fragmentation, polymerization and rearrangement of bonding, either inter- or intra- molecularly. Kinetically this could be gradually or suddenly, thermally it can be with varying amount of energy. The sudden and energetic ones need to be known if you are to work safely with them. Sensitivity to a stimulus such as heat, light, percussion, friction or chemical contact (usually acid) is the issue with those that rapidly produce energy. The reaction rate will increase with higher temperature, pressure or concentration.

Examining molecular structures, unobstructed double or triple bonds and strained rings can indicate potential polymerizability. An easy, logical electronic rearrangement to produce something simple and stable like nitrogen, oxygen or carbon dioxide, leaving the rest of the molecule stable, may indicate fragmentability. The presence of oxidizing functionality with electron rich functional groups that are easily rearranged to neutralize each other, can be a warning in an unfamiliar compound. The "bottom line" question: Is there a higher heat of formation arrangement of the atoms in a molecule and is there an easy way for them to get there?

Because reactive chemicals have a propensity to undergo vigorous, sometimes spontaneous, reactions and, under certain conditions, may spontaneously generate large quantities of heat, light, gases or toxic chemicals, work with reactive chemicals such as explosives, acid sensitives, oxidizers, reducers, water sensitives, and pyrophorics should be done only after understanding the possible reactions and potential energy release per mole.

15.1 Explosives

A material is classified as explosive if it produces a sudden, almost instantaneous release of pressure, gas and heat when subjected to abrupt shock, pressure or high temperature. Examples: "dry" picric acid (2, 4, 6-trinitrophenol), 2, 4, 6-trinitrotoluene (TNT) and nitroglycerine. Prior to procuring an explosive chemical or compound, PI's must file a Hazardous Material Procurement and Use Authorization (Form HMMP-A) with EHS.



15.1.1 Shock-Sensitive and Friction-Sensitive Explosives

Shock-sensitive explosives can spontaneously release large amounts of energy not only when struck, vibrated, dropped, heated, or otherwise agitated but also under normal conditions. Some chemicals become increasingly shock-sensitive with age. Of great concern in the laboratory is the inadvertent formation of shock-sensitive explosives such as peroxides in solvents and other materials that can be shock-sensitive explosives including:

- azides of hydrogen, ammonium, alkaline earth metals, copper, silver, mercury, thallium and lead

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- carbides and acetylides of copper, silver, gold and mercury
- nitrides of sulfur, selenium, tellurium, copper (Cu₃N), "fulminating" silver (Tollin's test and silvering solutions) and gold, and mercury (Millon's base, HgN-Hg-OH)
- alkyl azides from sodium azide in DMSO (or similar) and alkyl halides (CH₂Cl₂, dichloroethane)
- fulminates (:C=N-O) of hydrogen, ammonium, and metals (in general)
- fulminates of silver, mercury, thallium and lead formed from nitrates dissolved and heated in ethanol
- mercuric oxide - mercuric cyanide, silver cyanate, mercury(II) cyanate, (light sensitive) silver cyanamide (Ag₂N=C=N), (light sensitive) mercury(I) cyanamide
- oxalate and tartrate of silver and mercury
- hypophosphite (phosphinate, H₂P(0)O⁻) acid, aluminum, magnesium (heating disproportionates them to phosphine which can ignite), dipotassium phosphinate, KHP(0)OK (ignites in air if wet), and shock and temperature sensitive: -
copper(II) - silver - iron(III) manganese(II)- lead(II)
- RedOx salts like basic stannous nitrate fSn₃(OH)₄(NO₃)₂₁, ferrous perchlorate, guanidinium, hydrazinium, hydroxyl amine salts with: - nitrates -
perchlorates - chromates
- ammonium salts mixed with salts of: nitrite - chlorate - bromate -
permanganate
- hydroxylamine free base disproportionates when heated
- hydroxylammonium iodide and phosphinate
- metal salts of picric acid, dinitrophenol, dinitro resorcinol and nitromethane (aci-nitro anions)
- chlorite salts of
-lithium (heat) -nickel (heat / shock) -copper (shock)
-sodium (heat / shock) -lead (heat) -silver (heat/shock)
-barium (heat) - thallium(I) (shock) -mercury(I) & (II) (unstable)

15.2 Monomers

Under appropriate conditions, monomers undergo polymerization, in which the monomers combine with each other to form repeating structural units, or a polymer. If not controlled, polymerization can occur at a rate that releases large amounts of energy that can cause fires, explosions or burst containers. Examples: formaldehyde and styrene

This list is not inclusive. If you are in doubt as to the reactive or explosive potential of your chemical procedures, consult an authoritative reference such as Bretherick's Handbook of Reactive Chemical Hazards. The American Chemical Society has compiled an index of reported incidents of laboratory explosions that have appeared in Chemical and Engineering News. Call (800) 227-5558, for the ACS Health and Safety Referral Service for information.

Other laboratory shock-sensitives which may be encountered are perchlorates in fume hood ducts and azides in drain lines. It is important to distinguish between shock-sensitive and friction-sensitive compounds. Picric acid and ether peroxides are not especially shock-sensitive, however, opening a tight cap produces major frictional forces which can cause an explosion. If spilled on a concrete floor and not cleaned, picric acid will form calcium picrate, which is easily detonated by footsteps when dry.

Nitrate salts of metals, the oxides of which are water insoluble, if mixed and heated with nitric acid and ethanol can oxidize the ethanol to acetaldehyde and acetic acid, then nitrate

it, decarboxylate and dehydrate it to fulminic acid, $H-C=N-O$, and finally form the fulminate salt.

15.3 Organic Peroxides

There are many compounds that have "peroxide" in their name, some are hazardous, and some are relatively safe at ambient pressure and temperature. Organic peroxides are those organic compounds containing the bivalent $-O-O-$ structure. These chemicals are very unstable and may be explosive. A common organic peroxide is benzoyl peroxide.

Common Chemical Families Known to be Peroxide Formers

- Organics
 - Ethers, acetals.
 - Olefins with allylic hydrogens, chloro- and fluoro-olefins, terpenes, tetrahydronaphthalene. ○ Dienes, vinyl acetylenes.
 - Aldehydes.
 - Ureas, amides, lactams.
 - Vinyl monomers including vinyl halides, acrylates, methacrylates, vinyl esters.
- Inorganics
 - Alkali metals, particularly potassium
 - Alkali metal, alkoxides and amides
 - Organometallics.

15.3.1 Peroxide Formation

When a substance slowly reacts with oxygen from the atmosphere (i.e., autooxidation), there are several different reactions possible. Many peroxide-formers will slowly rearrange to non-peroxide oxidized forms and cause no trouble beyond their eventual lack of usefulness. Examples of these are: benzaldehyde and other aldehydes, amines, mercaptans, sulfides, N-alkyl amides and alkyl iodides. Other peroxide-formers will slowly polymerize and eventually become solid plastic. Examples of these substances include styrene, vinyl acetate and ethyl acrylate. Since these chemicals may be packaged in air, inhibitors of radical polymerization are added (hydroquinone, usually). But peroxides can form, and polymerization eventually occurs even if the container has not been opened. Most common in peroxide formation is that of soluble (i.e., they remain dissolved) hydroperoxides and ketone peroxides from secondary alcohols, ethers, tertiary carbons (as in decalin), and allylic and benzylic carbons (as in alkenes and alkyl benzenes). Manufacturers may add an inhibitor to peroxide forming chemicals to counter peroxide formation. For many peroxide-forming solvents, butylated hydroxy toluene (BHT) is commonly added. BHT 'scavenges' oxygen in the solvent and prevents it from reacting with the solvent to form peroxides. Over time, BHT or other inhibitor in the solvent can become exhausted allowing peroxides to form. Distilling the solvent can completely remove the BHT and make the solvent immediately susceptible to peroxide formation.

It is the organic peroxides that form unintentionally that are of great concern because of their unpredictability, explosivity, and often grave consequences. Once peroxides are formed, these chemicals can become extremely sensitive to thermal or mechanical shock and may explode violently. Peroxides are formed through a spontaneous reaction with oxygen. Simply opening the container can initiate peroxide formation, while light and heat act to accelerate the process. Peroxides form primarily in liquids but can also form in solids and even bottled gases that are liquefied under pressure.

15.3.2 To safely distill peroxidizable solvents:

- Eliminate the peroxides with a chemical reducing agent or pass the solvent through activated alumina.
- Add mineral oil to the distillation pot. This has the combined effect of "cushioning" any bumping, maintaining dilution and serving as a viscous reaction moderator in case the peroxides begin to decompose.
- Carefully monitor the distillation process to ensure that it does not dry out completely, and then overheat.
- To reduce peroxides during distillation
 - Add small pieces of sodium metal to the distillation vessel to reduce peroxides. Use benzophenone as an indicator for the presence of sodium metal (benzophenone, in the presence of sodium metal forms a radical with a deep-blue color). When the blue color disappears, add more sodium metal.
- Be wary of high peroxide levels and wary of cleaning a "spent" pot.

15.3.3 Testing Peroxide-forming Agents

CAUTION: Testing should ONLY be performed by a chemist properly trained in the procedure.

The following test procedures may be used on most organic solvents. However, there is not a suitable, simple test procedure for detection of peroxides in substances such as alkali metals, alkali metal alkoxides, amides, or organometallics.

Iodide Test Add 0.5-1.0 ml of the solvent to be tested to an equal volume of glacial acetic acid to which has been added about 0.1 g of sodium iodide or potassium iodide crystals. A yellow color indicates a low concentration of peroxide in the sample; a brown color indicates a high concentration. A blank determination should be made. Always prepare the iodide/acetic acid mixture at the time the test is made, because air oxidation slowly turns the blank to a brown color.

Ferrothiocyanate Test A drop of the solvent to be tested is mixed with a drop of sodium ferrothiocyanate reagent, which is prepared by dissolving 9 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in 50 ml of 18% hydrochloric acid. Add 0.5- 1.0 g granulated zinc followed by 5 g sodium thiocyanate. When the transient red color fades, add 12 g more of sodium thiocyanate and decant the liquid from the unused zinc into a clean, stoppered bottle. Pink or red coloration indicates the presence of peroxides.

Peroxide Test Strips Test strips are commercially available from several vendors. Fisher Scientific currently offers a potassium iodide/starch test strip. VWR offers more elaborate test kits manufactured by EM Science and J.T. Baker. Follow the manufacturer's instructions for using the strips/kits to ensure adequate colorimetric detection.

Results:

- 0-30 ppm (KI reagent turns slightly yellow): Little or no threat of violent reaction. Should be stabilized with hydroquinone, t-butyl catechol or ferrous sulfate (between 1 and 250 ppm or about 0.1 mg inhibitor/ Liter of solvent).

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- 30-80 ppm (KI reagent turns brilliant yellow): Expired or mismanaged compounds that may pose a threat to persons and structures. The available literature shows that attempts to stabilize these compounds may initiate exothermic reactions that may pose a threat to persons and structures. Tag the container for EHS Hazardous Waste pickup and contact EHS.
- Greater than 80 ppm: (K1 reagent turns brilliant yellow to red): Expired or mismanaged compounds that pose a threat to persons and structures. Do not attempt to stabilize. Tag the container for EHS Hazardous Waste pickup

15.4 Pyrophoric

Chemicals that ignite on exposure to air at temperatures of 54 °C (130 °F) or lower temperature are considered to be pyrophoric. Such chemicals can be gases, solid or liquid, volatile or non-volatile. What occurs is that oxygen, in its ordinary form, reacts with the chemical in the gas phase or on the surface in a way that leads to sustained combustion for as long as oxygen is present. This requires that the reaction is rapid enough and delivers enough energy to propagate a flame in the gas phase or release underlying atoms / molecules in condensed phase for the air to contact.

Pyrophoric chemicals can be elements or compounds. Some examples are boranes, hydrides (triethylaluminum, lithium aluminum hydride), and white or yellow phosphorus. Many alkali metallic powders (sodium, potassium) are pyrophoric. The degree of reactivity is primarily related to particle size. Solids are more susceptible if finely divided or somewhat volatile. Three distinct initiating events are possible:

- Oxygen binds to a metal atom, whether a lower valence transition metal compound (titanium(II) chloride), a covalent metal alkyl or hydride (triethylaluminum) or a transition metal finely divided.
- Oxygen binds to an unshared electron pair on an alkyl or hydro derivative of phosphorus, arsenic or antimony and
- Water in air combines with an alkaline metal ion that is in combination with hydride or alkylide (butyllithium), generating heat from creating a metal - oxide bond and protonation of the hydride or alkyl, which ignites the hydrogen or alkane in air.

Otherwise, an active metal binds water producing the metal oxide or hydroxide and hydrogen, which then ignites in the heat produced. Many active metals will react directly with oxygen and oxidize completely without igniting. Some pyrophoric reactions include:

- Some lower valence transition metal oxides and catalyst metal powders (palladium) can combine with oxygen in air producing a plume of hot nitrogen, but no other species that would glow to make the combustion visible, (i.e., a flame).
- White phosphorus, which will spontaneously ignite if warm, finely divided or damp in air will otherwise glow on air exposure from a slow reaction with oxygen that releases an intermediate's energy as phosphorescence.
- Unsaturated oils like linseed oil and hydrazine derivatives, methyl hydrazine, will react with oxygen if absorbed on cloth that allows enough air movement to supply oxygen but not so rapid as to carry away the heat of reaction, producing delayed spontaneous combustion.
- Phosphine at low concentrations in air will also glow (i.e., marsh gas).



- Hydrosulfite (dithionite) salts, if damp, but not dissolved in water will ignite due to the low-level presence of sulfur dioxide radical anion from sulfur to sulfur bond disassociation.

Prior to procuring a pyrophoric chemical or compound, PI's must file a Hazardous Material Procurement and Use Authorization (Form HMMP- A) with EHS.

15.5 Water Reactive

Water-reactive chemicals react violently with water, water vapor or moist air to produce heat and flammable hydrogen gas which can ignite. Alternately, the reaction can produce a toxic gas or other hazardous condition. It makes a big difference whether the moisture enters slowly, if water is thrown on the substance or if the substance is thrown into water. Usually water splashed or poured onto the material is the greatest hazard since fire or explosion may result from the reaction.

Examples of water-reactives include: alkali metals (e.g., lithium, sodium and potassium and their hydrides), calcium oxide, sulfur trioxide, silicon tetrachloride, anhydrous aluminum chloride, phosphorus pentoxide, trifluoromethanesulfonic anhydride, and chlorosulfonic acid.

In a world where water can be a solid, liquid, or vapor (i.e., air humidity), chemical water reactivity is an important safety consideration. When water reacts with some chemicals, unfortunate results are possible. These can range from:

- spontaneous ignition
- pressure building in a container
- violent heat production
- oxidation or reduction by water reaction
- toxic gas release
- chemical effectiveness lost by hydrolysis or hydration

There are eight basic physical and / or chemical reactions that water can initiate:

1. Reduce ionic charge density by either protonation of a small anion, including hydrogen bonding with hydroxide from a strong base, or becoming a ligand on a positive ion, including being protonated by a strong acid.
2. Coordination expansion of an atom by adding across a double bond (e.g., sulfur trioxide hydration to sulfuric acid).
3. Replacing a weaker ligand, such as hydrolysis of an acid chloride.
4. Oxidation of a metal or a lower valence state transition metal compound, producing hydrogen gas in the process.
5. Reduction of a strongly oxidizing compound (e.g., cobalt(III) fluoride), producing oxygen gas.
6. Hydration of a non-ionic compound by hydrogen bonding or hydration cage structure.
7. Deliquescence, that is, hydration to the point of forming an aqueous solution of the chemical from airborne humidity.
8. Solution in water, by ionic dissociation or hydrogen bonding.

The first five can be rather energetic and fast reactions, while the latter three are less exothermic and may even be endothermic, being entropically driven. With the energetic reactions, adding the compound to water can be safer than adding limited water to the

compound, simply because when you add it to water, the surrounding water will absorb the heat produced.

The water need not be liquid for the reaction. Water in air (i.e., humidity) can enter into a poorly closed container and react as well. Here the reaction is controlled by the diffusion rate of the air. Examples of unwanted reaction by air include:

- Calcium phosphide reacts slowly with humidity to produce phosphine and calcium hydroxide.
- Calcium carbide reacts to produce acetylene with enough heat to ignite the acetylene in air.
- Reaction with a non-alkaline metal halide or non-metal halide to produce hydrogen halide gas that, in the case of a small leak, diffuses out slower than the lighter air and water molecules can diffuse so pressure builds up in the container.
- The infamous reaction of aluminum and arsenic oxide (e.g., a ladder placed in a pit containing arsenic) which builds deadly arsine gas in a confined space, will not occur without a proton donor, which can be water from humid air.

16 Reproductive Agents

Some chemicals can cause damage to the reproductive systems of men or women leading to infertility, impotence, menstrual irregularities, spontaneous abortion or damage to offspring. Chemicals include heavy metals, some aromatic solvents (benzene, toluene, xylenes, etc.), and some therapeutic drugs.



Reproductive toxins are substances that cause chromosomal damage (mutagens) and substances with lethal or teratogenic (malformation) effects on fetuses. Embryo toxins or fetotoxins are substances that may be lethal to the fertilized egg, embryo or fetus, may be teratogenic (i.e., cause fetal malformations), may retard growth or may cause postnatal functional deficits. Male reproductive toxins can in some cases lead to sterility. Two well-known male reproductive toxins are ethylene dibromide and dibromo chloropropane.

No recognized comprehensive list of known human reproductive toxins exists. The Occupational Safety and Health Administration (OSHA) only regulates four agents based on their reproductive toxicity: lead, ionizing radiation, 1,2-dibromo-3-chloropropane (DBCP), and ethylene oxide.

Remember, toxicological data is lacking for many chemicals. This is especially true for data on the human reproductive health effects (especially related to the male). Most commercial chemicals and physical factors have not been thoroughly evaluated for their possible toxic effects on reproduction and development. Information on suspected reproductive health hazards is derived primarily from animal studies, which present problems of interpretation in extrapolating to effects in humans. Individuals also vary widely in susceptibility and extent of exposure to reproductive hazards. Proper handling of chemicals and use of protective equipment is effective in reducing fetal exposure to chemicals.

Persons working with teratogens and other reproductive health hazards and those who are contemplating pregnancy or are already pregnant should review the toxicity of the chemicals in their workplace and, if concerned, should consult with EHS and their personal physician

to determine whether any of the materials pose additional risk during pregnancy and possible means to reduce those risks.

16.1 Embryo toxins

Embryo toxins are substances that act during pregnancy to cause adverse effects on the fetus. These effects include death of the fertilized egg, the embryo, or the fetus, malformation, retarded growth and postnatal functional deficits. Examples of embryo toxins include organomercurials, lead compounds, and formamide.

16.2 Mutagens

A mutagen affects the genetic material of exposed cells. Mutations can occur on the gene level (gene mutations) as when one nucleotide base-pair is changed to another. Mutations can also occur on the chromosomal level (chromosomal mutations) when the number of chromosomal units or their morphological structure is altered. The effect is inherited by daughter cells and, if it occurs in the gonads or reproductive organs, can become part of the genetic pool that is passed on to future generations. Examples of mutagens commonly found in biomedical research laboratories include: ethidium bromide, barium permanganate, methyl isocyanate and radioisotopes.

16.3 Teratogens

Teratogens are materials that adversely affect a developing embryo or fetus. When a pregnant woman is exposed to a chemical, some chemicals can cross the placental barrier affecting the fetus. A developing fetus may be more sensitive to some chemicals than the pregnant mother, especially during the first twelve weeks of pregnancy when the mother may be unaware she is pregnant.

Teratogenic chemicals are those substances that cause fetal death or malformation from maternal exposure during pregnancy. These teratogens are agents which interfere with normal embryonic and fetal development without apparent damage to the mother or lethal effects on the fetus. Because cellular genetic effects are not produced, these effects are not hereditary. Known human teratogens include organic mercury compounds, lead compounds, 1,2-dibromo-3-chloropropane, ionizing radiation, some drugs, alcohol ingestion, and cigarette smoking. Some substances which may cause adverse reproductive effects in males include 1,2-dibromo-3-chloropropane, cadmium, mercury, boron, lead, some pesticides, and some drugs.

More than 800 chemicals have been shown to be teratogenic in animal models; many of these are suspected human teratogens.

16.4 Ethidium Bromide (EtBr)

Ethidium bromide is a powerful mutagen widely used in biochemical research laboratories for visualizing DNA fragments. It binds to single-, double- and triple-stranded DNA. Its primary mobility hazard is as a dust dispersed in air while being transferred as a powder from one container to another or while making solutions. Airborne dispersion is also a concern when cleaning spilled powder. Fortunately, ethidium bromide is brilliantly self-indicating in its intense color. Contact with skin will show.

There is no information on its rate of transport through skin. Mutagenic concentrations demonstrated effects on DNA separations in cell division in fruit flies at 1200 ppm and DNA damage in HeLa cells in culture at 16 ppm solution application. The threshold of noticeable

color is about 16 ppm. Thus, any contact that stains skin should be washed off with soap and water until the stain is removed. Seek immediate medical attention for dust inhalation that is at the level where color is seen in sputum or on a nose swab.

Ethidium bromide stains will bind to absorbents and gels so that these two times won't become sources of the dye. The sanitary sewer limit for ethidium bromide is 10 mg/L (see Chapter 7). Solutions disposed via sanitary sewer will rapidly dilute below hazard levels before treatment collection is reached. Non-permeable surfaces like glazed ceramics, metal and glass can be washed free of the dye and trashed, sharps can be disposed or reused, whichever is appropriate.

17 Select Agent Toxins

Select Agent Toxins are certain toxins of biological origin which are subject to stringent regulatory requirements under [42 CFR 73](#) for their potential to pose a severe threat to public, animal, or plant health, or to animal or plant products. These toxins, along with specified biological agents (viruses, bacteria, fungi), fall under the oversight of the National Select Agents Registry (NSAR) Program which requires registration for possession, use, and transfer of the listed Select Agents. However, possession of small amounts of Select Agent Toxins as described below is exempt from registration with the NSAR Program. See EHS for additional information.

17.1 Possession of Permissible Amounts of Select Agent Toxins

The following Select Agent Toxins are not regulated if the amount under the control of a principal investigator does not exceed, at any time, the amounts indicated in the table below.

Select Agent Toxins / HHS Toxins [§73.3(d)(3)]	Amount
Abrin	1,000 mg
Botulinum neurotoxins* (see note below)	1 mg
Short, paralytic alpha conotoxins	100 mg
Diacetoxyscirpenol (DAS)	10,000 mg
Ricin	1,000 mg
Saxitoxin	500 mg
Staphylococcal Enterotoxins (Subtypes A, B, C, D, and E)	100 mg
T-2 toxin	10,000 mg
Tetrodotoxin	500 mg

*Botulinum neurotoxin use in a research setting is also regulated by Dual Use Research of Concern. Please see the EHS website for more information.

Additionally, the following Select Agent Toxins are excluded:

- Any Select Agent Toxin that is in its naturally occurring environment provided it has not been intentionally introduced, cultivated, collected, or otherwise extracted from its natural source.
- Nonfunctional Select Agent Toxins as defined by the [Federal Select Agent Program](#).

Use of these Select Agent Toxins in permissible amounts requires strict adherence to UCCS's requirements that address critical safety and compliance information including safe use, storage/security, and inventory management.

17.2 Possession of Select Agent Toxins Above Permissible Amounts

Possession of Select Agent Toxins in amounts above permissible amounts requires prior approval from the Vice Provost and Dean of Research and registration with the National Select Agent Registry Program. Also note, that effective 12/4/12, botulinum neurotoxins are categorized as Tier 1 agents, which trigger additional regulatory requirements.

Failure to register with the NSAR Program is potentially punishable by up to five years in prison and/or large monetary fines. (*Public Health Security & Preparedness Response Act of 2002, Section 231(c), 18 USC 175(b), & Public Law (USA Patriot Act) 107-56 Sec. 817*).

18 Toxics

A toxic is any chemical that, when ingested, inhaled or absorbed, or when applied to, injected into, or developed within the body in relatively small amounts, by its chemical action may cause damage to biological structure and/or disturbance of biological function.

The biological effects – whether beneficial, indifferent or toxic – of all chemicals are dependent on several factors, including:

- Dose (the amount of chemical to which one is exposed)
- Duration of exposure (both length of time and frequency)
- Route of entry:
 - Ingestion
 - Absorption through the skin
 - Inhalation
 - Injection
- Individual response and history
- One's exposure to other chemicals
- Mixing the toxin with other chemicals



NOTE: Inhalation and dermal absorption are the most common methods of chemical exposure in the workplace.

The most important factor in toxicity is the dose-time relationship. In general, the more toxin to which an individual is exposed, and the longer they are exposed to it, the stronger their physiological response will be. However, an individual's response can also depend on several other factors, including:

- Health
- Gender
- Genetic predisposition
- An individual's exposure to other chemicals
- Previous sensitization
- Chemical mixtures

NOTE: When a person becomes sensitized to a chemical, each subsequent exposure may often produce a stronger response than the previous exposure.

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NOTE: Combining a toxic chemical with another chemical can increase the toxicity of either or both chemicals.

IMPORTANT: Minimize exposure to any toxic chemical.

Damage can also be acute (immediate) or chronic (delayed). Acute toxicity is the effect manifested on short exposure or single contact. Chronic toxicity is the effect observed when a toxic substance acts on the body over time. This can be due to multiple or continuous exposure.

Examples of acute toxins include the following:

- Hydrogen cyanide
- Hydrogen sulfide
- Nitrogen dioxide
- Ricin
- Organophosphate pesticides
- Arsenic

IMPORTANT: Do not work alone when handling acute toxins. Use a fume hood to ensure proper ventilation or wear appropriate respiratory protection if a fume hood is not available.

Examples of chronic toxins include the following:

- Mercury
- Lead
- Formaldehyde

Damage can be local (direct) or systemic (indirect). Local toxicity is the effect of a substance on the body area that has been exposed to the substance. Systemic toxicity is the effect of a substance on body tissue after absorption into the bloodstream.

Many systemic toxins are organ or system specific and can be classified as:

- Hematotoxins. Chemicals that affect blood cells or hematopoietic system (e.g., bone marrow). Examples include: nitrites, benzene, toluidine, aniline and nitrobenzene.
- Hepatotoxins. Chemicals that damage the liver. Examples: ethanol, carbon tetrachloride., nitrosamines, and 1,1,2,2-Tetrachloroethane
- Nephrotoxins. Chemicals that damage the kidneys. Examples: chloroform, carbon tetrachloride, halogenated hydrocarbons and uranium compounds.
- Neurotoxins. Chemicals that affect the central or peripheral nervous system. The nervous system is especially sensitive to organometallic compounds and certain sulfide compounds. The damage produced may be permanent or reversible. In many instances, detection of neurotoxic effects may require special exams, but effects can sometimes be inferred from behavior such as slurred speech or staggered gait. Many of these neurotoxic agents may be chronically toxic substances whose effects are not immediately apparent. Examples of neurotoxic agents include:
 - trialkyl tin compounds
 - methyl mercury
 - tetraethyl lead
 - carbon disulfide
 - thallium

- manganese
- organophosphate insecticides (malathion, parathion, Vapona)

18.1 Mercury

Mercury is a naturally occurring metal that has several forms. Metallic mercury is the familiar heavy, shining, silver-white liquid at room temperature. If heated, it becomes a colorless, odorless gas. Mercury also vaporizes at room temperature, though at a slower rate. Mercury metal is one of the noble metals. It is quite stable to oxidation and occurs naturally, in some cases, as the metal. The oxide is easily decomposed to mercury vapor at — 500 °C. The metal is uniquely volatile for a metal; vapor pressure is 2.5×10^{-3} mm Hg at ambient temperature. This may seem to be a low pressure to be calling mercury "volatile," but the hazards of breathing and skin absorption at that concentration are real.

Mercury IS KNOWN TO BE TOXIC to humans, especially young children and unborn babies. However, mercury is not a health threat when safely encased.

Many commercial products and items contain metallic mercury and/or mercury compounds. Mercury-containing products are regulated as hazardous waste for disposal. All mercury-containing products and items must be turned in to Environmental Safety for proper disposal.

Examples of items that can contain mercury include:

- **Thermostats.** Many temperature control devices contain an ampoule of mercury metal. When replacing defective thermostats select a digital type replacement, which does not use mercury. Do not attempt to disassemble a mercury-containing thermostat or otherwise disturb the housing. Package the entire unit in a plastic bag for pick-up by Environmental Safety.
- **Fluorescent and High Intensity Bulbs.** Some fluorescent, neon, mercury vapor, high-pressure sodium, metal halide, and high intensity lamps contain regulated quantities of mercury. These items must be properly disposed via the Universal Waste (Recycling) Coordinator in Facilities Management or Environmental Safety.
- **Batteries.** Certain types of batteries contain significant amounts of mercury and must be turned in to Environmental Safety for proper disposal.
- **Thermometers, Manometers, Sphygmomanometers, etc.** Replace mercury-based equipment with digital or organic liquid-based equipment whenever possible. Never use mercury thermometers in ovens or other heat producing equipment.
- **Electrical Switches and Dials.** Some electrical switches and dials contain mercury. Care should be taken to prevent breakage or leakage of mercury when removing these types of items from service; leave them intact and bag in plastic for pick-up by Environmental Safety.
- **Paints.** Prior to 1991, mercury was incorporated into some paint formulations as a biocide agent. Mercury-containing paints and related items (i.e., brushes, rags, etc.) must be bagged in plastic and turned in to Environmental Safety for proper disposal.
- **Agricultural Products.** A very limited number of agricultural fungicides contain Mercury. Mercury-containing fungicides must be returned to the distributor or bagged in plastic and turned in to Environmental Safety for proper disposal.

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Mercury spilled on the floor in a room will not result in equilibrium vapor pressure in any reasonable amount of time. Undisturbed evaporation of a 10 cm diameter pool of mercury is estimated at 0.1 jig/sec, which gives very low levels of vapor in lab air.

Noticeable mercury exposures will occur whenever a thermometer bulb is broken and trapped in a rug that is then walked on. Vapor can be plumed into the air and will accumulate if the ventilation rate is very slow, as is the case in an air tight house in the winter. People who constantly work in the contaminated space will need a few months to accumulate a hazardous blood level. However, mercury accumulation can be drastically hastened if a vacuum cleaner sucked the mercury from a rug or floor and blew warm air over it while it was in the collection bag. Vacuuming could thus throw the whole amount into the air during the time the machine is running. Because the person vacuuming would be breathing at an elevated level, they could rapidly intake a large quantity.

High surface tension and poor "wetting" ability of liquid mercury makes handling drops of the liquid generally safe. Transdermal diffusion will occur when the skin is stained with a dispersion of the metal. People can be poisoned if they rub the metal into their skin and leave it on for a while.

Mercury compounds are a totally different case. A notable example is the case of the mobile, volatile and penetrating dimethyl mercury. A few drops that can rapidly absorb into the skin of the hands can lead to slow death over months. Skin whitening cream that have used mercury chloride as an ingredient have slowly invaded the user's system and produced toxic symptoms. A few tenths of a gram of mercury in the body as a burden, whether rapidly acquired or slowly, can be lethal.

18.1.1 Routes of Exposure

Mercury may enter the body through inhalation, ingestion or skin absorption and cause serious damage to many systems of the body. Once in the bloodstream metallic mercury travels to other parts of the body, including the brain and kidneys, and can remain in these organs for months.

18.1.2 Health Effects

Mercury health effects are cumulative

- Mercury causes damage to the nervous system and brain -- unborn and young children are most vulnerable because their nervous systems are still developing.
- Mercury also causes damage to the kidneys, liver, stomach, respiratory system, intestines, and increases blood pressure and heart rate.
- Skin contact can cause an allergic reaction resulting in skin rashes.
- Contact with the eyes can cause severe irritation.
- Swallowing mercury can cause nausea, vomiting and diarrhea.
- Mercury vapor causes damage to the lining of the mouth and lungs. High levels of mercury vapor exposure can cause death.
- Mercury exposure can result in
 - General fatigue,
 - Tremors,
 - Insomnia,
 - Weakness,
 - Memory loss,
 - Headaches,
 - Irritability,



- Nervousness,
- Changes in hearing and vision,
- Emotional disturbance, and
- Unsteadiness.

18.2 Lung (Pulmonary) Toxic Agents

Some agents cause damage to the pulmonary tissue (lungs) by means other than immediate irritant action. Fibrotic changes can be caused by free crystalline silica and asbestos. Other dusts (e.g., coal dust, cotton dust, wood dust and talc) can cause a restrictive disease called pneumoconiosis.

18.3 Synthesized Chemicals

Some laboratories synthesize or develop new chemical substances during the course of their research. For the safe handling and management of a newly synthesized chemical, the researcher must label the substance with the IUPAC name or a clearly identifiable lab-designated name; a chemical structure may be included as well. Also, label the substance with the material's hazardous properties (e.g., toxic, reactive, flammable, corrosive), determined to the best of the researcher's ability. If the composition of a new chemical substance or mixture is unknown, it must be assumed to be hazardous.

If the lab transfers newly synthesized chemicals to another user outside of the university or if any adverse health or environmental effects are observed by laboratory personnel working with newly synthesized chemicals, contact EHS at 719-255-3212 for assistance.



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- ¹ Attach the applicable Safety Data Sheet to this form.
- ² Attach annotated floor plan indicating storage location and NFPA marking.