C_001 - Chemical Safety Training

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LLE Chemical Hygiene Officer
About this training

• Description:
  - Review of UR’s Chemical Hygiene Program; Safe work practices; Hazardous communications, SDS (MSDS); Personal protective equipment, and Hazardous Waste Management

• Required participants:
  - Persons who work in a laboratory with chemicals, hazardous materials and solvents, or persons who handle, work with, store or dispense chemicals, hazardous materials and/or solvents

New personnel *must* obtain signature of Chemical Safety Officer after completing quiz
Achieving and maintaining a safe working environment is everyone’s responsibility

**Administration**
- Establish safety guidelines and protocols
- Ensure regulatory compliance and employee safety

**Principal Investigators (P.I), work area supervisors**
- Provide task-specific and material-specific training
- Promote safe working conditions and practices: 
  - lead by example

**Employees**
- Learn hazards before beginning experiments
- Follow safety protocols in every experiment
- Identify and report potentially hazardous situations to the appropriate P.I, work area supervisor, or LLE Safety Officer
Training topics

- Identifying, classifying, and storing hazardous materials
- Overview of gas cylinder safety*
- Hazard communication
  - accessing chemical safety information
  - Globally Harmonized System of Classifying and Labelling of Chemicals (GHS) transition
    - Safety Data Sheets (SDS)
    - labeling
- Exposure minimization
  - engineering controls
  - safe work practices
  - Personal Protective Equipment (PPE)

*Covered in-depth in M_002, Compressed Gas Safety Training
Training topics

• Dealing with chemical emergencies

• Site specific safety procedures
  - beryllium
  - lead
  - formaldehyde
  - high pressure liquid nitrogen fill station

• Hazardous waste
  - sharps management
  - waste accumulation
  - disposal
Hazardous materials pose significant physical or health risks under normal laboratory use

**Physical**

- Flammable
  - Acetone
- Combustible
  - Kerosene
- Corrosive
  - Hydrochloric acid
- Oxidizer
  - Chlorine bleach
- Explosive, unstable, reactive
  - perchlorates, lithium metal

**Health**

- Carcinogens, teratogens (causes birth defects), mutagens (causes genetic mutations)
  - Formaldehyde
- Toxic
  - Hydrogen cyanide
- Irritant
  - Ammonia
- Sensitizer
  - Beryllium dust
- Target organ effects
  - Chloroform

Radioactive Material Safety is covered in the *R_002 Safety Training*
OSHA standard 29 CFR 1910.106(a)(19) defines the terms *flash point, flammable and combustible*

- **Flash point** – the minimum temperature at which a liquid will produce a sufficient concentration of vapor within a test vessel to form an ignitable mixture with air near the liquid surface when a small flame is introduced.

- **Flammable** liquids are defined as those that have a flash point below 100°F (37.8°C).

- **Combustible** liquids are defined as those that have a flash point above 100°F (37.8°C)

```
Flammable < 100°F (37.8°C) ≥ Combustible
```

Organic peroxides undergo auto-accelerated thermal decomposition and are excluded from these flashpoint determinations.
Flammables are separated into four categories according to their flash points and boiling points

**Category 1 (extremely flammable):**
- Flash point < 73.4°F (23°C)
- Boiling point ≤ 95°F (35°C)

**Ex: Diethyl ether**

**Category 2 (highly flammable):**
- Flash point < 73.4°F (23°C)
- Boiling point > 95°F (35°C)

**Ex: Toluene, acetone**

**Category 3 (Flammable liquid and vapor):**
- Flash point ≥ 73.4°F (23°C) and ≤ 140°F (60°C)

**Ex: Acetic acid, acetylacetone**

**Category 4 (Combustible liquid):**
- Flash point ≥ 100°F (37.8°C) and ≤ 199.4 °F (93 °C)

**Ex. Kerosene, chloroform**
Explosion and fire are the two primary hazards associated with flammable and combustible liquids

- Many organic solvents are *highly flammable*
- Common organic solvents include (but are not limited to):
  - Acetonitrile
  - Benzene
  - Ethanol
  - Isopropyl alcohol
  - Methyl ethyl ketone
  - Toluene

Always review safety information and work in a fume hood when using organic solvents
Hazardous materials must be stored in separate locations according to their *hazard class*

### Hazard classes include:

- Flammables
- Inorganic acids (nitric acid and perchloric acid are powerful oxidizers and are stored separately)
- Bases
- Organic acids (acetic acid, formic acid)
- Oxidizing agents
- Reducing agents
- High health hazard materials
  - carcinogens
  - teratogens
  - mutagens
  - acutely toxic
Flammable solvent storage outside of an approved storage cabinet is limited to 8 gallons

- Both insulation and self-closing, air-tight doors provide high fire resistance

All flammable solvents in excess of the 8-gal. limit must be stored in approved flammable solvent storage cabinets
Storing items on top of a flammable storage cabinet is a violation of NYS Fire Code

**WARNING**

**FIRE HAZARD**

Storing items on top of flammable storage cabinet could increase fire risk
Do Not Place Anything On Top of This Cabinet

Ensure that the tops of all flammable storage cabinets remain clear of any items
Ethers and certain alcohols form *highly unstable peroxides* upon prolonged exposure to air and/or light.

- Peroxides can be **explosive** if heated or allowed to evaporate to dryness!
- Solvents that generate peroxides include diethyl ether, tetrahydrofuran (THF), dioxane, butanol, pentanol and other secondary alcohols

**Peroxide-forming materials must be:**
- tested for peroxide content every 6 months
- containers labeled with both the date received and the most recent peroxide test date
Supervisors and P.I.’s are responsible for ensuring that peroxide-forming materials stored in their areas are tested for peroxide content every 6 months.

1. Dip test strip into test solution for approximately 1 second:

2. Gently shake off excess liquid:

3. Wait 5 seconds:

4. Compare the test paper zone with the color scale:

5. Keep Dispose
Both full AND empty gas cylinders must be secured upright to an immovable object at all times

- Cylinders must *never* be double strapped

All persons working with compressed gas must complete M_002, Compressed Gas Safety Training
Flammable gases must be stored at least 20 ft away from any oxidizing gases or gas mixtures

- Flammable gases and gas mixtures must be:
  - used and stored in a well-ventilated area that is readily accessible in case of emergency
  - electrically grounded to prevent sparks and static charge buildup

Spark-proof tools must be used when changing regulators
Gas cylinders must be transported upright using only approved cylinder carts.

Remove regulators and replace cylinder valve caps before transporting to avoid damage to cylinder shut-off valves.
Special caution must be taken when working with cryogenic liquids and associated equipment

- Glass vacuum Dewar flasks can shatter if filled too rapidly with liquid nitrogen
- Pressure relief valve (PRV) failures can cause catastrophic damage and injury

*NEVER* replace, modify, shut off, or tamper in any way with PRV’s on cryogenic containers
Facility-wide chemical safety information at LLE is available both on-line.

http://safety.lle.rochester.edu/530_chemical/msds.php

Example: Searching for physical properties and safety information

Access is limited to users with an LLE computer account
and in hard-copy format in the LLE Safety Library (Rm 1414)
Each LLE laboratory or work area must have its own set of laboratory-specific materials safety data.

- Safety documentation must be **prominently displayed and rapidly accessible**; these items include:
  
  - The Chemical Hygiene Plan (CHP) binder
    - CHP document
    - Chemical inventory
    - SDS’s (for laboratories with a small chemical inventory)
  
  - (Material) Safety Data Sheets (MSDS) binder
    - one or more volumes for laboratories with a large chemical inventory

All employees must know the location of the CHP and Safety Data Sheet binders in their work areas.
Chemical labeling and storage requirements are transitioning from the National Fire Protection Association (NFPA) to the Globally Harmonized System (GHS)

- OSHA has adopted new hazardous chemical labeling requirements to align with the United Nations’ Globally Harmonized System of Classification and Labeling of Chemicals. These changes will:
  - Ensure improved quality and consistency in the classification and labeling of all chemicals
  - Enhance worker comprehension
  - Provide better information on the safe handling and use of hazardous chemicals
  - Prevent injuries and illnesses related to exposures to hazardous chemicals
All manufacturers, distributors, employers and employees must be in complete compliance with GHS by June 1, 2017

- **HCS 2012 published in Federal Register**
- **All employers must complete initial training on GHS labeling and SDS**
- **Grace period ends for manufacturers and distributors to use older HCS 1994 labeling**


- **HCS 2012 goes into effect**
- **Manufacturers and distributors must begin using GHS-compliant labeling for all shipping products**
- **Employers must begin updating GHS workplace labeling and training (begins 1 yr. grace period)**

**Transition period**

HCS* 1994, GHS (HCS 2012), or both

* HCS – Hazard Communication Standard
Chemical manufacturers must provide SDS documents in a standardized 16-section format by 1 June 2015

Material Safety Data Sheets (MSDS)

1. Product identification / name
2. Hazard identification
3. Composition / Information on ingredients
4. First aid measures
5. Fire fighting measures
6. Accidental release measures
7. Handling and storage
8. Exposure controls / personal protection

Safety Data Sheets (SDS)

1. Product identification / name
2. Hazard identification
3. Composition / Information on ingredients
4. First aid measures
5. Fire fighting measures
6. Accidental release measures
7. Handling and storage
8. Exposure controls / personal protection
9. Physical / chemical properties
10. Stability and reactivity
11. Toxicological information
12. Ecological information
13. Disposal considerations
14. Transportation information
15. Regulatory information
16. Other information
Categories define the level of hazard within a given hazard class. Example 1: Acute Oral Toxicity

<table>
<thead>
<tr>
<th>Hazard Class: ACUTE ORAL TOXICITY</th>
</tr>
</thead>
<tbody>
<tr>
<td>Category 1: <strong>Severe hazard</strong></td>
</tr>
<tr>
<td>Category 2: <strong>Serious hazard</strong></td>
</tr>
<tr>
<td>Category 3: <strong>Moderate hazard</strong></td>
</tr>
<tr>
<td>Category 4: <strong>Slight hazard</strong></td>
</tr>
<tr>
<td>Category 5: <strong>Minimal hazard</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>LD&lt;sub&gt;50&lt;/sub&gt; (mg/kg)*†</th>
</tr>
</thead>
<tbody>
<tr>
<td>Larger LD&lt;sub&gt;50&lt;/sub&gt; = lower toxicity</td>
</tr>
<tr>
<td>&lt; 5</td>
</tr>
<tr>
<td>&gt; 5 &lt; 50</td>
</tr>
<tr>
<td>&gt;50 &lt; 300</td>
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<tr>
<td>&gt;300 &lt; 2000</td>
</tr>
<tr>
<td>&gt;2000 &lt; 5000</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Pictogram</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Image]</td>
</tr>
<tr>
<td>[Image]</td>
</tr>
<tr>
<td>[Image]</td>
</tr>
<tr>
<td>No symbol</td>
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<table>
<thead>
<tr>
<th>Signal word</th>
</tr>
</thead>
<tbody>
<tr>
<td>Danger</td>
</tr>
<tr>
<td>Danger</td>
</tr>
<tr>
<td>Danger</td>
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<tr>
<td>Warning</td>
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<tr>
<td>Warning</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Hazard statement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fatal if swallowed</td>
</tr>
<tr>
<td>Fatal if swallowed</td>
</tr>
<tr>
<td>Toxic if swallowed</td>
</tr>
<tr>
<td>Harmful if swallowed</td>
</tr>
<tr>
<td>May be harmful if swallowed</td>
</tr>
</tbody>
</table>

*LD<sub>50</sub> = Median lethal dose: the amount of a toxin, radiation, or pathogen (expressed in mg/kg of body weight) required to kill 50% of the members of a test population after a specified test duration.†

†Created by J.W. Trevan in 1927, the LD<sub>50</sub> test has been phased out. The U.S. Food and Drug Administration has begun to approve non-animal alternatives to LD<sub>50</sub> in response to research cruelty concerns and the lack of validity/sensitivity of animal tests as they relate to humans[1].

Categories define the level of hazard within a given hazard class. Example 2: Flammable liquids

<table>
<thead>
<tr>
<th>Hazard Class: FLAMMABLE LIQUID</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Category 1: Severe hazard</strong></td>
</tr>
<tr>
<td>Flash point (°C)*</td>
</tr>
<tr>
<td>Boiling point (°C)</td>
</tr>
<tr>
<td>Pictogram</td>
</tr>
<tr>
<td>Signal word</td>
</tr>
<tr>
<td>Hazard statement</td>
</tr>
</tbody>
</table>

*Flash point = lowest temperature at which the material is ignitable in the vapor state

*Sub-categories also exist for certain specific chemical classes (e.g. explosives, self-reacting materials, peroxides)*
NFPA and GHS graphical warning labels provide rapid communication of critical safety information

Both the NFPA and GHS systems will be in simultaneous use over the transition period.

The GHS will supercede (but not entirely replace) the NFPA system as employers transition to the new standard.
The numerical hazard classification rating scales for the GHS and NFPA systems are opposite!

**NFPA**
- Severe = 4
- Serious = 3
- Moderate = 2
- Slight = 1
- Minimal = 0

**GHS**
- Cat. 1 = Severe
- Cat. 2 = Serious
- Cat. 3 = Moderate
- Cat. 4 = Slight
- Cat. 5 = Minimal

Use *extreme caution* when interpreting label or SDS information.
The GHS mandates standardized labels on all hazardous materials containers.

Product identifier

Signal Word

Hazard statements

Precautionary statements

Pictograms

Company Name, Street Address, City, State, Zip, Country Phone number
Signal words discriminate between hazard levels

“Danger” implies a higher hazard level than does “Warning” (“Caution” and “Notice” are not used in the GHS)
**Pictograms** communicate chemical hazards

- **Flame:** *Flammables*  
  * Self-Heating  
  * Self Reactives  
  * Organic Peroxides  
  * Pyrophorics  
  * Emits Flammable Gas

- **Exploding Bomb:** *Explosives*  
  * Self Reactives  
  * Organic Peroxides

- **Flame over Circle:** *Oxidizers*

- **Skull & Crossbones:** *Acute Toxicity*  
  (fatal or toxic)

- **Health Hazard:** *Carcinogen*  
  * Respiratory Sensitizer  
  * Reproductive Toxicity  
  * Target Organ Toxicity  
  * Mutagenicity  
  * Aspiration Toxicity

- **Gas Cylinder:** *Gases Under Pressure*

- **Corrosion:** *Corrosives*  
  * Irritant  
  * Dermal Sensitizer  
  * Acute Toxicity (harmful)  
  * Narcotic Effects  
  * Respiratory Tract Irritant

- **Exclamation Mark:** *Acute Aquatic Toxicity*
Hazard statements provide succinct, critical information on the nature of the hazard and/or its severity.

**Hazard statement**

**Specific hazards associated with the material, regardless of how it is used.**

**Hydrofluoric acid**

**DANGER**

Fatal if inhaled, if swallowed, or in contact with skin. Causes severe skin burns and eye damage. Effects may be delayed. Do not eat, drink or smoke when using this product. May be corrosive to metals.

**PREVENTION**

Do not breathe mist or vapors. Use only outdoors or in a well-ventilated area. Where exposure limits are exceeded, wear respiratory protection. Do not get in eyes, on skin, or on clothing. Wash skin and eyes thoroughly after handling. Wear protective gloves and clothing, and eye and face protection. Keep only in original container.

**RESPONSE**

Immediately call a doctor or other medical personnel.

If swallowed: Rinse mouth. If in eyes: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing. If on skin (or hair): Take off immediately all contaminated clothing. Wash skin with water or shower. Wash contaminated clothing before reuse. Contaminated skin must be treated with calcium gluconate solution. If inhaled: Remove person to fresh air and keep comfortable for breathing. Absorb spillage to prevent material damage.

**STORAGE**

Store in corrosive resistant container with a resistant inner liner. Store locked up. Keep container tightly closed.
Precautionary statements give guidance on safe work procedures and handling protocols.
Chemical storage and container labeling will transition to the new GHS format

- Container label:

- Cabinet label:
Labeling for hazardous materials containers must be *clearly legible and unambiguous*

- Re-used/recycled chemical containers MUST have all old labels covered or removed!
- Rubber stopper is not acceptable
- Labels are damaged and/or not legible
- No label
Recycled food containers for are *not acceptable* for hazardous materials storage.

Can corrode and leak

No label
Hazardous materials may enter the body by four different routes of exposure

<table>
<thead>
<tr>
<th>Low</th>
<th>Exposure probability</th>
<th>High</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ingestion</td>
<td>Injection</td>
<td>Skin/eye contact</td>
</tr>
</tbody>
</table>

- The level of exposure can have widely varying health effects for different people

- Exposures can be:
  - **Acute**: brief, high concentration (e.g., cleaning up a spill)
  - **Chronic**: extended over days or weeks (e.g., cleaning parts with solvent)

- Health effects from exposure can be reversible or irreversible, depending on the materials toxicology

- Individuals can respond differently to the same exposure (e.g., allergies)
OSHA has established inhalation exposure levels below which adverse health effects normally do not occur

- **Permissible exposure limit (PEL)**: the limit on the amount or concentration of a substance in the air based on an 8-hour time weighted average (TWA) exposure

- **Short-term exposure limit (STEL)**: the acceptable average exposure over a short period of time, usually 15 minutes as long as the TWA is not exceeded

- **Ceiling limit**: the concentration of a chemical or material that no person should be exposed to for any period of time to prevent ill effects or death

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Exposure minimization is the most effective means for preventing adverse health effects

Exposures are best prevented through a combination of:

- **Engineering controls**: the first line of defense in minimizing exposure potential. Both the work environment and the job should be designed to eliminate hazards or reduce exposure to hazards to the extent feasible.

- **Safe work practices**: these practices include general workplace and other operation-specific rules.

- **Administrative controls**: measures beyond safe work practices aimed at reducing exposure to hazards.

- **Personal Protective Equipment (PPE)**: used when exposures cannot be eliminated completely by engineering controls and administrative controls cannot provide sufficient protection.

For many hazardous materials, there are NO established exposure limits; personnel should use *maximum caution* when working with unknowns.
Experimental activities must be designed and conducted with exposure minimization and containment in mind
Engineering controls keep the concentration of hazardous contaminants within known OSHA exposure limits

- **Fume hoods** are often the primary control device for protecting laboratory personnel working with flammable and or toxic chemicals

- **Glove boxes** are used when the toxicity, radioactivity, or air sensitivity of the substance pose too great a hazard for use in a fume hood

- Check regularly – leaks will contaminate the lab environment

Working with hazardous materials in an open and uncontrolled environment should be avoided whenever possible
Proper fume hood use is essential in maintaining laboratory safety

- Make sure the sash is open to the proper operating level (indicated by arrow)

- Keep all materials inside the hood at least six inches from the sash opening

Fume hoods should never be used for long-term storage of chemicals
Proper fume hood use is essential in maintaining laboratory safety

• **Before using a fume hood:**
  - understand its functional controls and how they work
  - know the hazards of the chemical(s) that will be used
  - ensure the hood exhaust is on, functioning and the air flow is within the required range (above 100 lineal ft/min)

• **When using the fume hood:**
  - never allow your head to enter the plane of the hood opening when experiments are in progress
  - always wear chemical safety eye wear
  - make sure nothing is blocking the air flow baffles at the rear of the hood

Safe work practices are employed as an additional means of reducing exposure risk

• Exposures can still occur even when a hazard is contained

• Examples of safe work practices for specific OSHA standards include (but are not limited to):

  ➢ Respiratory protection – all respirator users must be certified through UR Respirator Wearers Program (UHS) annually

  ➢ Lockout/Tagout (LOTO) – prevents operation of equipment that could cause injury or equipment damage. LLE instructions 3000 and 6300 defines LLE-specific policies
The Chemical Hygiene Program promotes safe work practices by a number of different means

- Provides standard operating procedures and control measures to reduce employee exposure to hazardous chemicals
- Classifies chemical hazards and mandates communication of these hazards to both employers and employees
- Requires a facility-wide chemical inventory to identify the locations and quantities of hazardous materials to aid in mitigation of accidents and spills

Work habits make the single largest impact on both your safety and that of the people working around you.
Poor work habits are one of the leading causes of laboratory accidents

the bad . . .
Ignorance of materials hazards and proper procedures can result in catastrophic accidents

... and the ugly

Supervisors and P.I.’s set the standard for safe working habits in their areas!
The majority of chemical laboratory accidents are caused by *poor work practices: Incident “A”*

- During an undergraduate organic chemistry lab class, a student poured a small quantity of waste material into a hazardous waste collection bottle.
- Moments after the student walked away, the container exploded in the hood.
- Because the student had remembered to lower the hood sash, the explosion was contained and no one was injured.
The majority of chemical laboratory accidents are caused by *poor work practices*: Incident “B”

- A graduate student was slicing potassium metal in a toluene-filled dish next to a sink
- A fragment of potassium fell into the damp sink
- Hydrogen generated by reaction of potassium with water was ignited by heat of reaction, which then ignited the toluene
- *The student received superficial first-degree facial burns, but no other injuries*
Eating and drinking in laboratory and work areas is strictly prohibited.

- Food and drink consumption in laboratories and work areas greatly increases the risk of accidental ingestion of hazardous materials.
PPE requirements are determined by both the hazards of the material and the process in which it is used

- PPE is provided by LLE and usage is mandatory when indicated
- Work area supervisors and P.I.’s must:
  - provide appropriate PPE in their work areas
  - enforce wearing of required PPE
- PPE must:
  - fit properly and be inspected at each use for flaws, proper fit, and function
  - must meet ANSI standards
- Section 8 of the GHS standard 16-section format SDS provides guidance on each chemical’s PPE requirements

Maintenance (cleaning) and care of PPE is the responsibility of the employee
Eye protection and gloves are *mandatory* for *all* chemical operations at LLE

Chemical safety eyewear must bear the American National Standards Institute (ANSI) Z87.1-1989 approval marking

Eyewear requirements:
- provide adequate protection against hazards
- fit snugly and not interfere with movements of the wearer
- be reasonably comfortable
- be durable
- be capable of being easily disinfected and cleaned

Regular prescription glasses *DO NOT* provide adequate protection
The eyes can be rapidly and irreversibly damaged by even a momentary contact with certain materials

- Safety “glasses” are the minimum acceptable protection for working with chemicals

- Safety goggles provide better protection against splashes and solvent vapor and are required for contact lens wearers

- A full face shield is required when working with corrosive chemicals that can burn the skin

- Even with a face shield, safety eyewear is still necessary
Selection of the proper glove material and thickness is critical for minimizing potential exposures

**Disposable gloves:**

- Use for incidental contact with low toxicity materials
  - latex and PVC are poor choices
  - nitrile rubber or chloroprene provide better protection

**Reusable gloves:**

- Use for repeated and/or prolonged exposure with moderately toxic materials

**Insulated gloves:**

- Use for working with high temperature operations or with cryogenics

Inspect gloves carefully for holes or rips before use
Proper donning and doffing of gloves is necessary to prevent cross-contamination

1. Pinch the outside of the glove near the wrist (careful not to touch exposed skin below)
2. Pull glove up *slowly*, turning the glove inside out
3. Ball up the used glove and grasp it with the gloved-hand
4. Using non-gloved hand, put finger inside cuff of glove
5. Pull glove up *slowly*, turning glove inside-out *and* encapsulating the balled glove
6. Finish removing glove and dispose of properly
Remove gloves before touching keyboards, telephones, door handles or leaving the work area.

Chemical burns, skin irritation, or other exposures can occur if contaminated gloves come in contact with the skin (i.e. scratching an itch).
Laboratory coats and aprons provide additional protection against splashes and spills

- Laboratory coats made of 100% cotton provide secondary protection from minor exposures
- Rubber aprons and boots may be needed for larger scale processes or highly corrosive materials

Do not launder lab coats at home - use a commercial laundry service!
Flame resistant (FR) lab coats are required where pyrophoric materials are used

- **Pyrophoric materials** can spontaneously ignite in air and will react vigorously with water or high humidity, often igniting upon contact

- Flame resistant lab coats:
  - must have FR label
  - be made with Nomex (fire resistant material)
  - polyester coats are NOT suitable

- Fires involving pyrophoric materials generally require a **Class D** fire extinguisher
In 2008, a research assistant died from injuries sustained in a chemical fire in a laboratory at UCLA: Incident “C”

- The researcher was working with tert-butylithium (t-BuLi) when the syringe plunger came out of the barrel and the t-BuLi was exposed to the atmosphere

- The t-BuLi ignited and a nearby flask of hexane caught fire, igniting the workers clothes

- She was wearing safety glasses and nitrile gloves, no lab coat and a polyester blouse

- Her clothing from the waist up was largely burned and melted into the skin. Large blisters formed on her abdomen and hands - She passed away 18 days later
In 2008, a research assistant died from injuries sustained in a chemical fire in a laboratory at UCLA

- OSHA concluded the accident was a result from safety lapses and inadequate training. Criminal charges were brought against both UCLA and the student’s supervisor

- The supervisor settled out of court and paid $10,000 and was required to participate in community service

- What could have been done to prevent the incident?
  - Safety and emergency training for laboratory personnel
  - Utilization of safety shower
  - Use smaller reagent volumes
  - Use of Nomex lab coat

The clothing you wear when working in the laboratory is an important part of your personal protective equipment—dress appropriately for the task at hand
Respirators are deployed in special circumstances only and are **NOT** a substitute for engineering controls

**All** respirator users must be certified through UR Respirators Wearers Program (UHS)

- **Initial certification**
  - Medical history form
  - Physical exam and spirometry test
  - Respirator fit test

- **Annual re-certification**
  - Verify medical history
  - Repeat respirator fit test

- The OMEGA and OMEGA EP target chambers are beryllium-regulated areas and require respiratory protection for entry

**Report respiratory problems / issues in work areas to your supervisor or the Chemical Hygiene Officer**
Eyewash and safety showers must be accessible in or near all areas where chemicals are stored, used or handled

Safety eyewashes and showers must:

- be located within 55 feet (10 sec) from the hazard
- supply clean, potable water
- remain clear of obstructions
- be flushed on a regular basis
  - eyewashes: 1x weekly for 3-5 min (laboratory personnel)
  - showers: 1x every 6 mos. for 3-5 min (assigned personnel)
- have a log with recorded flush dates near each unit

All personnel must know the location of the emergency units in or near work areas
Laboratory personnel are responsible for flushing eyewash stations in their areas and recording flushing dates in the eyewash logs.

- The Chemical Safety Co-op provides new eyewash logs and archives full logs.
If a chemical spill or emergency occurs, contact the work area supervisor and a safety officer immediately.

**Minor spills**
- Clean up using a spill control kit
- Dispose of absorbed material as hazardous waste

**Major spills/ injuries/ emergencies**
- During *working* hours call LLE reception:
  - 55101 or 53941
- *After* hours:
  - 13 – for UR Public Safety
  - 9-911 if no response on 13

**After hours protocols**
- Minimum of two people present when conducting a chemical process (buddy system)
- Supervisor permission is *required for* anyone working after hours

If a chemical exposure (e.g. eyes or skin) occurs flush the affected area immediately and notify the P.I. and a safety officer.
Special procedures and training are required when working with certain hazardous materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Hazard</th>
<th>Mitigation</th>
<th>Training requirements</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Beryllium</strong></td>
<td><strong>CBD, Cancer suspect agent</strong></td>
<td>Wet crimp cutting (no drilling or machining) Designated work areas Respiratory protection</td>
<td>C_002: Beryllium Safety Training (annual)</td>
</tr>
<tr>
<td><strong>Lead</strong></td>
<td><strong>Dust</strong></td>
<td>No drilling or machining Cover large items (shielding bricks) with tape and label</td>
<td>“Lead Encapsulation Procedure” (V 1.0, 6/10/09) (one-time)</td>
</tr>
<tr>
<td><strong>Formaldehyde</strong></td>
<td><strong>Carcinogen, allergic sensitizer</strong></td>
<td>Use in fume hoods only with proper PPE</td>
<td>C_003: Formaldehyde Safety Training (annual)</td>
</tr>
<tr>
<td><strong>Liquid Nitrogen (High pressure fill station)</strong></td>
<td><strong>High LN2 delivery pressure, Cryogenic burns</strong></td>
<td>Safe operation training</td>
<td>C_004: High Pressure Liquid Nitrogen Fill Station – one-time proficiency operational demonstration</td>
</tr>
</tbody>
</table>
Repeated exposure to beryllium particles is a risk factor for both **Chronic Beryllium Disease (CBD) and cancer**

- **CBD**: is an irreversible lung disease produced by a sensitization (allergic) reaction to beryllium particles
- **Beryllium dust has recently been determined to cause cancer in humans**
- Beryllium is used in both OMEGA and OMEGA EP as vacuum windows, x-ray filters, blast shields, and target supports
- **LLE Instruction 6706** establishes procedures to insure safe handling and exposure minimization
  - prohibits any beryllium shaping processes that can generate dust *(sawing, drilling, abrading)*
  - beryllium articles can only be shaped by *wet crimp cutting*

**Employees that work with beryllium must complete the**
**LLE C_002 Beryllium Safety Training**
Lead dust can be harmful if inhaled or ingested

- Lead enters the body primarily through inhalation and ingestion
- When inhaled as dust, lead passes through the lungs into the bloodstream where it can harm many of the body’s organ systems

- Follow the steps in the Lead Encapsulation Procedure (V 1.0, 6/10/09) to reduce the risk of exposure

- Drilling or machining of lead is prohibited at LLE

All lead bricks must be fully encapsulated and labeled
Exposure to formaldehyde can result in serious acute and chronic health effects

- OSHA’s Formaldehyde Standard (29 CFR 1910.1048) mandates procedures and protocols for working with formaldehyde beyond those outlined in the Chemical Hygiene Plan (CHP). These include:
  - special container labeling
  - limits on amounts of formaldehyde stored, depending on concentration
  - a written spill control countermeasure plan in areas where formaldehyde is used
  - protocols for decontamination of clothing
  - medical surveillance for individuals exposed to airborne formaldehyde concentrations of 0.75 ppm (8 hr TWA) or 2-ppm (15 min STEL)

Employees working with formaldehyde must complete the LLE C_003 Formaldehyde Safety Training
Use of the LLE high pressure liquid nitrogen filling station (LN2) is limited to trained individuals

- The training process is “hands-on” and is conducted by either a certified fill station operator or the LLE Chemical Hygiene Officer (CHO)

- A “certified” fill station operator is one who has:
  - successfully completed the LLE Mechanical Safety (M_001), Compressed Gas Safety (M_002), and Chemical Safety (C_001) trainings
  - received initial training from the CHO in the safe operation of the fill station
  - conducted at least two filling operations under the close supervision by a certified certified fill station operator
  - demonstrated both proficiency in operating the fill station and a working understanding of safety rules by conducting a filling operation unaided while being observed by the CHO

Users must complete LLE C_004 High Pressure Liquid Nitrogen Fill Station Safety Training before operation
The high-pressure LN2 fill-station is intended for filling closed, PRV-equipped cryogenic containers ONLY

- Certified users can obtain the fill station key from the West Lobby receptionist
- Users name MUST be on the certified users list to sign out the key - no third party designates
- Fill station key must be returned by no later than 5:00 PM.

Operation of the high pressure fill station after hours requires the permission of both the CHO and the Chief Safety Officer; a buddy must also be present for the duration of the fill
Open cryogenic containers must ONLY be filled from the 160 L low-pressure storage dewar

- Users must complete the LLE M_001 General Mechanical Safety and M_002 Compressed Gas Safety Trainings before handing cryogenic liquids
Hazardous chemical waste disposal is governed by EPA and NYSDEC regulations

- Hazardous chemical waste is defined as any chemical-containing product, item or material that is unwanted or has no further use and is
  - **Ignitable**: solvents, oils
  - **Corrosive**: acids, bases, developers, metal etchants
  - **Toxic**: heavy metals, cyanides, carcinogens
  - **Reactive**: oxidizers, reducing agents, air-sensitive compounds
  - **Unstable**: catalysts, peroxides, perchlorates

- **Hazardous waste disposal information** can be found at the LLE Safety Zone (http://safety.lle.rochester.edu/530_chemical/disposal.php)

Other hazardous wastes (radioactive, biological) are covered by different regulatory agencies
Nearly everyone working at LLE handles or generates some form of hazardous chemical waste

- Many items commonly used in laboratories qualify as hazardous chemical waste under the EPA guidelines:
  - batteries: *(toxic, corrosive, reactive)*: lead-acid, mercury, NiCd, NiMH, Li+, AgO - but NOT alkaline or carbon batteries
  - “sharps” *(toxic)*
  - “universal wastes” *(toxic)*: mercury-containing lamps, bulbs, switches, electronics
  - “E-waste” *(toxic)*: computers, power supplies, electronics
  - beryllium, lead and other powdered metals *(toxic, ignitable)*
  - aerosol cans *(ignitable, corrosive, toxic)*
Contact with chemically contaminated “sharps” can result in some of the most serious exposure injuries

- Syringe needles (new or used)
- Razor blades/scalpels
- Broken glass items (including optics)
- Microscope slides
- Pipettes

- Use approved sharps containers - *NEVER put sharps in the regular trash!*
Use *non-biohazard* sharps containers or glass disposal boxes to dispose of syringes, needles, razor blades, or other small sharp objects.

Special containers can be requested for biohazard items.
Syringe needles should \textit{NEVER} be bent, sheared, or re-capped using two hands - either during use or before disposal

- \textbf{Serious or possibly fatal exposure could occur, depending on the material contained in the syringe or needle}

- \textbf{Alternative: one-handed “scoop” technique}
  - place needle cap on table
  - hold syringe only, guide needle into cap
  - lift syringe so that cap is sitting on needle hub
  - secure needle cap in place

- \textbf{Better: use a safety needle}
  - mechanism to blunt or cover the needle after use
  - one-handed operation
Proper management and disposal of hazardous chemical wastes is the responsibility of those who generate them

- **Disposal requirements:**
  - identify by name, quantity and composition
    
    _NO UNKNOWNS_ are permitted
  - collect according to _hazard class_

- **Drain disposal of chemicals requires special permits**

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**Strong acids and bases**

**Volatile Organic Compounds (VOC’s)**

**Heavy metals**

**Water-insoluble organics**

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**UR Environmental Compliance / Hazardous Waste Office 275-2056**
EPA mandates specific requirements for hazardous waste storage in laboratories and work areas

• Storage areas *must* be labeled as:

```
HAZARDOUS WASTE SATELLITE ACCUMULATION AREA

Ignitable, corrosive, reactive, toxic, and other noxious chemical wastes must be disposed of as directed by the Hazardous Waste Management Unit. EPA & Monroe County regulations prohibit drain disposal, trash disposal, or the intentional evaporation of such wastes. If you have any questions concerning the disposal of chemical wastes, contact the hazardous Waste Management Unit at x5-2056.

All Hazardous Waste Containers must be:
- Labeled “Hazardous Waste” and state the chemicals contained within the bottle. A running log of what is placed into the container with quantities must be attached to the container at all times.
- Free of old labels. All other labels on waste containers must be removed.
- Compatible with the wastes placed into them.
- Kept closed when not actually adding to their contents.
- Placed into secondary containment. Non-compatible wastes must be kept separate. Do not mix wastes. Waste containers may not be located in sinks.
- Clean. Remove chemical residue immediately from the outside of the containers.

Variations are unacceptable!
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• Labels are available in the Safety Library (Rm. 1414)
Waste containers must be kept closed and stored in the labeled accumulation area except when being filled.

Secondary containment equal to 110% of the waste containers volume is required to control spills or container leaks.

Incompatible wastes (i.e., oxidizers and organic liquids) must be segregated.
Proper management and disposal of hazardous waste follows a multi-step process:

1. Is the waste hazardous?
   - Yes: Select container.
   - No: Date container, place in appropriate cabinet.

2. If hazardous:
   - Sewer or landfill disposal as appropriate.

3. If not hazardous:
   - Label container, record contents.
   - Transport to LLE main hazardous waste storage area.
   - Generate tracking tag.

Date container, place in appropriate cabinet.
Determine if the material to be disposed of qualifies as hazardous waste

- **Ignitable**: solvents, oils, organic liquids, paint strippers
  - Batteries
- **Corrosive**: acids and bases, photoresist developers, metal etchants
  - Sharps
  - Universal wastes
- **Toxic**: heavy metals, organometallics, cyanides, carcinogens, teratogens
  - E-waste
  - Beryllium
- **Reactive**: lithium, sodium, oxidizers, reducing agents, air-sensitive compounds and catalysts
  - Aerosol cans
- **Unstable**: peroxides, perchlorates
Container selection depends on both the physical properties and quantity of waste disposed

Must be chemically compatible with leak-free closure

Glass bottles

Heavy-walled plastic containers

Metal cans and drums

All materials except HF

HF-containing materials, other corrosives, solids

Non-corrosive liquids and solids

“Recycled” containers must be *triple-rinsed* before disposal or when re-used for hazardous waste storage
Improper hazardous waste container labeling is one of EPA’s most frequently issued citations

- Use **ONLY** the pre-printed *Hazardous Waste Accumulation Record* labels:

```
<table>
<thead>
<tr>
<th>Date added</th>
<th>Chemical(s) / Water</th>
<th>Amount added</th>
</tr>
</thead>
<tbody>
<tr>
<td>3/1/08</td>
<td>Hydrochloric Acid / Water</td>
<td>250 mL</td>
</tr>
<tr>
<td>3/4/08</td>
<td>Hydrochloric Acid / Water</td>
<td>350 mL</td>
</tr>
</tbody>
</table>

Total volume/weight: 600 mL
```

- Accumulation record labels are available:
  - LLE main hazardous waste storage area
  - Safety Library (Rm 1414)
  - LLE Safety Zone:
Three UR graduate students were injured in an explosion on River Campus: Incident “D”

- A glass container was being used to collect hazardous waste
- Residual organic material was present in the waste container
- Nitric acid waste was added to the container
- A chemical reaction created a rapid pressure build up, causing failure of the glass waste container
- Emergency crews recovered pieces of a container that contained a mixture of hydrochloric, nitric and sulfuric acids
  - **Nitric acid is a strong oxidizer and can react even with trace quantities of organic materials**
Hazardous waste tracking tags are generated using the information on the accumulation record.

- Tracking tags are available at:
  - LLE main hazardous waste storage area
  - Safety Library (Rm 1414)

Both the original waste ID label AND the tracking tag MUST be on the container before removal from the laboratory.
Transport properly filled and labeled containers to the main LLE hazardous waste storage area for pickup by the UR HWMU.

- Waste labels, date stickers
- Corrosives, oxidizers
- Batteries, sharps, universal wastes
- Small containers (1 gal max)
- Large containers (5 gal max)
- Aerosol cans
- Secondary containment required when transporting glass containers

Weekly waste pickups are scheduled for Thursday afternoons.
All waste containers must be “date-stamped” before placing in the appropriate hazardous waste cabinets

• By law, all waste containers must be removed by HWMU within 90 days of the “accumulation date”

Accumulation date

Month/day/year

Waste labeling supplies are located in the red-box in the Hazardous Waste accumulation area

DO NOT leave empty containers or those with unidentified contents in the cabinets!
Any deficiencies in the disposal process will result in rejection of the waste by HWMU and require corrective action by the waste generator.
Achieving and maintaining a safe working environment is everyone’s responsibility!

- “Human Factors” are responsible for the majority of accidents involving hazardous materials

- Learn material-specific hazards before starting experiments

- Make exposure minimization and containment your “S.O.P.”

- Use proper-fitting PPE in every experiment every time

- Avoid risky, “quick and dirty” procedures to save time

- Know what to do and who to call when something goes wrong

*When uncertain about proper procedure or operational safety: STOP and ASK!*
You have completed the C_001 training – but there is still **one more thing**......

*Complete the on-line quiz for C_001 and follow instructions when you receive your grade by email.*