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Cryogens and Dry Ice SOP

Summary

- Small amounts of liquid or solid can expand into very large volumes of gas. The main hazards include explosions, asphyxiation and oxygen deficiency, cold burns, frostbite, adhesion, boiling and splashing, and embrittlement of containers.
- Cryogenic liquids and dry ice should be stored and handled in well-ventilated areas to prevent excessive buildup of gas. Only transport cryogenic liquids in insulated dewars specifically designed for this purpose.
- Wear a face shield over safety glasses/goggles, loose fitting cryogenic gloves, lab coats, long pants, and closed-toe shoes for dispensing liquids.

What are cryogens and dry ice?

Cryogens, such as liquid nitrogen and helium, are liquefied gases that are kept in their liquid state at very low temperatures. Cryogens have boiling points below – 73 °C (- 100 °F) at 14.7 psia (an absolute pressure of 101kPa). The most common cryogens used at UMass are liquid nitrogen and liquid helium, which are odorless, tasteless, and colorless. Dry ice is frozen carbon dioxide; carbon dioxide is both an asphyxiant (meaning that it can displace oxygen) and actively toxic at high concentrations. Although not a cryogen, dry ice or solid carbon dioxide, which converts directly to carbon dioxide gas at – 78 °C (- 109 °F), is often used in laboratories. Different cryogens become liquids under different conditions of temperature and pressure, but all have two properties in common: they are extremely cold, and small amounts of liquid can expand into very large volumes of gas. For example, liquid nitrogen has a liquid to gas volume expansion ratio of about 700:1, and that for liquid helium is slightly higher (757:1).

Source: http://blogs.umass.edu/biogeochem/photos/imag0125/

Liquid helium is commonly used for nuclear magnetic resonance (NMR) or superconducting magnet cooling and ultra-low temperature research. Liquid nitrogen is also used for NMR and superconducting magnet cooling, and also for cold traps, tissue preparation, liquid nitrogen freezers and miscellaneous cooling purposes. Dry ice is used with solvents for cold baths, tissue preparation, shipping of temperature sensitive materials, and miscellaneous cooling purposes. Cryogens are also used to cool optics, detectors and inner shields of instruments, such as cryogenic spectrometers (CRSP) and charged coupled devices (CCD). Cryogens, as well as dry ice, can be hazardous if not handled properly.

What are the hazards?

Cryogens and dry ice can expand 700 to 900 times their volume upon boiling/sublimation, which may cause:

- Explosion: A cryogenic liquid or dry ice in a closed vessel will produce an increase in pressure on warming, which can cause explosive container failure. Depending on the contents of the vessels or vials, the explosion may pose chemical or biological hazards in addition to the direct physical hazard.
- Asphyxiation and oxygen deficiency: The boil-off gas may displace sufficient oxygen to cause a hazardous, or even lethal, reduced oxygen atmosphere. Oxygen levels below 19.5% are problematic.

Cryogens and dry ice are extremely cold, which may cause:

- Cold burns and frostbite: Tissue damage may be sustained after contact with the fluids, surfaces cooled by the fluids, or by evolving gases.
- Adhesion: The cold surfaces of equipment can cause skin to stick to the surface. Skin can tear in an attempt to remove it from the surface.
- Embrittlement: Many materials become brittle and fail due to contact with extremely low temperatures. Only use materials specially designed for cryogens and dry ice, such as dewars. Materials such as carbon steel, certain plastics, and rubber become brittle at these temperatures.
- Boiling and splashing: Cryogens may boil violently and splash when first added to a warm container.

Other hazards:

- Condensation of liquid oxygen: Using liquid nitrogen as a cold trap coolant may cause condensation of liquid oxygen which can lead to explosions and fires.
- Obscured vision: Condensed water vapor formed near cryogens can collect on the floor to produce a fog that can be difficult to see through.
- Noise: Noise can be produced when filling dewars due to expulsion of gas from the supply cylinder and flash evaporation through the transfer line and holding dewar.
- Implosion of dewars: Most dewars are constructed of double-layered glass with an evacuated interior to provide a thermal barrier to surroundings. Stress and damage to the glass can cause the dewar to implode. Some dewars are constructed out of foam material that does not pose this hazard (such as those available from Chemglass), and EH&S encourages the use of these whenever possible.

Occupational Exposure Limits

Cryogens:

Although nitrogen and helium are inert and do not have associated permissible exposure limits (PELs) or threshold limit values (TLVs), they are simple asphyxiants. While normal atmosphere contains between 20.8 and 21 percent oxygen, OSHA defines as oxygen deficient any atmosphere that contains less than 19.5 percent oxygen, and as oxygen enriched, any atmosphere that contains more than 22 percent.

Dry ice/Carbon dioxide:

- ACGIH Threshold Limit Value (TLV): 8-hour Time Weighted Average (TWA): 5,000 ppm; 15 min Short Term Exposure Limit (STEL): 30,000 ppm.
- OSHA Permissible Exposure Limit (PEL): Table Z-1 8-hour Time-Weighted Average: 5,000 ppm.

Please refer to OSHA 1910.1000 Table Z-1 (https://www.osha.gov/laws-regs/regulations/standardnumber/1910/1910.1000TABLEZ1), and ACGIH® 2020 Threshold Limit Values.

What Activities Could Pose a Risk?

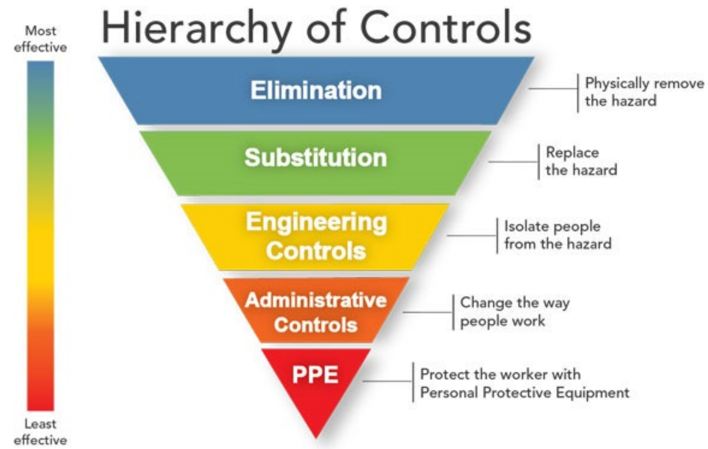
Cryogens and dry ice can be hazardous in labs when handling or dispensing improperly, including, but not limited to, the following activities:

- Storing cryogens or dry ice in cold rooms or poorly ventilated areas. Note that most cold rooms recirculate air and do not provide exhaust or fresh supply air. Use of cryogens in these spaces could rapidly produce an oxygen deficient environment.
- Handling or dispensing cryogens without proper PPE or unattended.
- Eye or skin contact with cryogens and their vapors or dry ice, such as handling cooled samples with bare hands.
- Placing cryogens on tile or laminated counters, which may destroy the adhesives.
- Storing cryogens or dry ice in a sealed, airtight container, which can lead to explosion.
- Tampering with pressure relief devices on equipment designed for cryogen use or storage.
- Allowing excessive ice buildup on equipment or dewars. This can lead to equipment failure and create puddles or sources of water contamination as it melts.
- Use defective equipment with cryogens or dry ice. Always check dewars for evidence of damage before using.

How Can Exposures Be Minimized?

When working with cryogens and dry ice, or any other hazardous material, always conduct a thorough risk assessment and employ the hierarchy of controls to minimize risk. Some specific applications of the hierarchy of controls to the hazards of cryogens and dry ice are listed below.

Always apply the controls in the order of most effective to least effective (see graphic), and apply as many controls as possible to reduce the risk to the lowest achievable level.



Elimination/Substitution

- Limit the amount of cryogens or dry ice stored and used in labs.
- Replace flammable cryogens or oxygen with other inert or less hazardous gases whenever possible.
- If using cryogens with solvents to make dry ice-solvent slurries for cooling, choose the least hazardous solvent with appropriate freezing point for your application.

Engineering Controls

- Cryogenic liquids and dry ice should be stored and handled in well-ventilated areas to prevent excessive buildup of gas. They should never be used in a closed environmental chamber.
- Use a stainless flex hose to dispense or transfer cryogens. Use of rubber tubing for this purpose is not appropriate as it can become brittle and break, leading to exposures.
- Do not alter or damage pressure relief valves.
- Only containers that are designed for use with cryogenic liquids should be used for this purpose. Containers designed to contain cryogens should have loose fitting lids to allow for pressure relief and provide thermal insulation.

Stainless flex hose

Dewar plug

Dewars

Administrative Controls

- Periodic inspection of equipment to store and dispense cryogenic liquids should be routinely performed.
- Do not hold the container during filling. It should be placed on the floor or a stable stand so that the transfer hose rests securely inside the neck of the secondary container so that it does not tip over during filling.
- Withdraw liquid slowly at first because the interior of the flask may still be at room temperature and rapid boil off will occur leading to excessive splashing.
- Do not fill to more than 80% of capacity to protect against possible thermal expansion of the contents and bursting of the vessel by hydrostatic pressure. Never fill containers higher than the indicated level.
- When using cryogenic liquids to cool an object, insert the object slowly using tongs and/or forceps while wearing cryogenic gloves. This procedure minimizes any boiling and splashing which occurs when warm objects are added rapidly.
- When possible, use a freight elevator to transport cryogenics. If cryogens must be transported in a passenger elevator, do not ride with the dewar. Have a colleague wait on the destination floor to retrieve the dewar, and place a sign on the dewar stating that no one should ride in the elevator with it.
- Immediately re-cap any open containers with cryogens after use to prevent atmospheric moisture from entering and forming an ice plug.
- Do not store containers where they may come into contact with moisture. Moving parts, such as valves or pressure relief devices, can malfunction due to external ice formation.
- Do not store cryogens or dry ice for long periods in an uncovered container.
- Never lower your head inside a dry ice chest or cooler. Carbon dioxide is heavier than air and will collect in the container producing an oxygen deficient atmosphere.

Personal Protective Equipment

- Wear a face shield over safety goggles, to protect eyes and face from splashes and vapors.
- Wear loose fitting cryogenic gloves to protect the hands. Gloves should be loose fitting so that quick removal is possible if liquid should splash into them. Even with gloves, contact with cryogens or dry ice should be for a very brief time. Do not submerse your gloved hands into a cryogenic liquid.

- Protective clothing should consist of lab coats, long pants, and closed-toe shoes to protect against skin contact in the event of a splash or spill.

<u>Waste Handling</u>

Share excessive cryogens and dry ice with your colleagues as much as possible. Do not dump cryogens on the floor for disposal. If material must be disposed of, allow the material to boil/sublimate in a fume hood. Coordinate with vendors for prompt return of empty dewars.

Do not dispose of cryogenic liquids or dry ice down the sink. When cryogens or dry ice hit the water, they will expand and the pressure will break the drain and pipeline. In addition, the material that a sink or plumbing fixture is composed of may not withstand the cryogens or dry ice temperatures and will become brittle and crack. Please contact EH&S at 413-545-2682 if there is accidental release to the drain.

<u>Exposure and Spill Procedure</u>

Exposures to cryogens or dry ice or spill should follow the general procedures for exposures and spill to hazardous materials outlined in the University's Chemical Hygiene Plan.

<u>References and Additional Resources</u>

1. OSHA: Quick Fact Sheet for Cryogens and Dry Ice. https://www.osha.gov/Publications/laboratory/OSHAquickfacts-lab-safety-cryogens-dryice.pdf
2. Air Products: Safetygrams. http://www.airproducts.com/company/Sustainability/environment-health-and-safety/product-safety-safetygrams.aspx
3. University of Pennsylvania, SOP: Cryogens and Dry Ice. https://ehrs.upenn.edu/health-safety/lab-safety/chemical-hygiene-plan/standard-operating-procedures/sop-cryogens-and-dry
4. University of Southern California: SOP-Cryogens and Dry Ice. https://ehs.usc.edu/research/lab/sop/sop-cryogens-and-dry-ice/

5. Lawrence Berkeley National Laboratory: ES&H Manual, Chapter 29: Safe Handling of cryogenic liquids. http://www.lbl.gov/ehs/pub3000/CH29/CH29.html
6. Harvard University: Lab Safety Guideline: Liquid Nitrogen and Argon. https://www.ehs.harvard.edu/sites/ehs.harvard.edu/files/lab_safety_guideline_liquid_nitrogen_and_argon.pdf
7. University of California, Berkeley: Safe Handling of Cryogenic Liquids. https://chemistry.berkeley.edu/research-safety/manual/section-7/cryogenic-liquids
8. Canadian Centre for Occupational Health and Safety: Cryogenic Liquids – Hazards. https://www.ccohs.ca/oshanswers/chemicals/cryogenic/cryogen1.html