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Laboratory Safety Guideline

Cryogenic Liquids

Introduction

Cryogenic liquids are liquefied gases having boiling points of less than –73.3ºC (-100ºF). The primary hazards of cryogenic liquids include both physical hazards such as fire, explosion, and pressure, but also health hazards such as chemical toxicity or severe frostbite and asphyxiation.

Not only are some liquid cryogens flammable in gaseous phase but some are very strong oxidizers and under the right conditions, inert cryogenic gasses may condense oxygen from the atmosphere. This oxygen-rich environment in combination with organic, flammable, or combustible materials may be particularly hazardous.

Pressure is also a hazard because of the large volume expansion ratio from liquid to gas that a cryogen exhibits as it warms and the liquid evaporates. This expansion ratio also makes cryogenic liquids more prone to splash and spatter, therefore skin and eye contact may occur. Contact with living tissue can cause frostbite or thermal burns, and prolonged contact can cause blood clots that have very serious consequences. All laboratory personnel should follow prudent safety practices when handling and storing cryogenic liquids.

Properties

The table below lists the boiling point and expansion ratios for some common cryogenic liquids.

Gas	Boiling Point (ºC)	Volume Expansion Ratio
Argon	-185.7	847-1
Carbon Dioxide	-78.5	553-1
Fluorine	-187.0	888-1
Helium	-269.0	757-1
Hydrogen	-252.7	851-1
Methane	-161.4	578-1
Nitrogen	-195.8	696-1
Oxygen	-183.0	860-1

Storage

- Work and storage areas should be well ventilated. Evaporation of the liquid cryogens will displace oxygen in the room and may present an asphyxiation hazard. Air contains about 21% oxygen and breathing air with less than 18% oxygen can cause dizziness and result in unconsciousness and death.

  Note: The cloud that appears when liquid nitrogen is exposed to air is condensed moisture in the atmosphere. Gaseous nitrogen is invisible.

- Cryogenic liquids should be handled and stored in containers that are designed for the pressure and temperature to which they may be subjected. The most common container for cryogenic liquids is a double-walled, evacuated container known as a Dewar flask.

- Containers and systems containing cryogenic liquids should have pressure relief mechanisms.

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- Cylinders and other pressure vessels such as Dewar flasks used for the storage of cryogenic liquids should not be filled more than 80% of capacity, to protect against possible thermal expansion of the contents and bursting of the vessel by hydrostatic pressure. If the possibility exists that the temperature of the cylinder may increase to above 30ºC (86ºF), a lower percentage (i.e. 60% capacity) should be the limit.
- Dewar flasks should be taped or shielded with mesh to minimize flying glass and fragments should an implosion occur.
- Dewar flasks should be labeled with the full cryogenic liquid name and hazard warning information.
- Never modify pressure relief valves on cryogenic cylinders. Pressure relief and occasional venting of gas is necessary to prevent over pressurization and explosion of cryogenic cylinders.

Handling

- Handle cryogenic liquids carefully. The extremely low temperatures can freeze human flesh rapidly. When spilled on a surface the liquid tends to cover the surface completely. The gas issuing for the liquid is also very cold. Delicate tissue such as the eyes can be damaged by the cold which may be too brief to damage the skin.
- Never allow unprotected parts of your body to touch any objects cooled by liquid cryogens. Unprotected body parts in contact with vessels or pipes that contain cryogenic liquids may bond firmly to the skin and tear flesh if separation is attempted.
- Use tongs or proper gloves to handle objects that are in contact with cryogenic liquids.
- Appropriate personal protective equipment should be worn when handling cryogenic liquids. This includes special cryogen gloves, safety goggles, full-face shield, impervious apron or coat, long pants, and high topped shoes. Gloves should be impervious and sufficiently large to be readily removed should a cryogen be spilled. Watches, rings, and other jewelry should NOT be worn.

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- Precautions should be taken to keep liquid oxidizers (i.e. oxygen) from contacting organic materials; spills on oxidizable surfaces can be hazardous. Do not use grease on any oxygen equipment, fittings, or containers.
- Keep all equipment clean. Keep storage areas clean and free of moisture or conditions that could damage or corrode containers.
- Transfers or pouring of cryogenic liquid should be done very slowly to minimize boiling and splashing. Use a phase separator or special filling funnel to prevent splashing. The top of the funnel should be partially covered whenever possible to shield splashes.
- Use small Dewars that are easily handled to transfer liquids. Use a cryogenic liquid withdrawal device for larger quantities from heavy containers.
- Keep Dewars upright and avoid rough handing. Do not transport Dewars in closed vehicles.
- Do not overfill containers. Overfilling above the neck tube can cause overflow when the neck tube core or cover is placed in the opening.
- Never use hollow tubes as dipsticks. When a warm tube is inserted into the cold liquid the liquid will spout from the top of the tube due to the rapid expansion of liquid cryogen inside the tube. Wood rods or solid metal dipsticks are recommended. Plastic rods will become very brittle.
- Keep cryogenic liquids and dry ice used as refrigerant baths open to the atmosphere. They should never be used in a closed system where they may develop uncontrolled or dangerously high pressure.
- Do not transfer liquid hydrogen in an atmospheric air environment. Oxygen from the air can condense in the liquid hydrogen presenting a possible explosion hazard.
- Never dispose of liquid cryogens in confined spaces or drains. Liquid nitrogen can be slowly poured onto gravel outside where it will evaporate safely without causing damage.

Refrigerator Contents

Materials stored in liquid cryogens are protected by the extremely cold temperatures of the liquid or the gas from the liquid. When all the liquid has evaporated the temperature will slowly rise to ambient temperature. The rate of evaporation depends on the design of the container as well as the age and condition of the container. Evaporation rate increases as the insulation efficiency decreases with age. Frequent opening and closing of the container will also increase the evaporation rate.

- Check the liquid level at least once a week.
- Refill with enough liquid to last until the next scheduled refilling.
- Keep the liquid level high enough to cover materials that must be kept at liquid temperatures.
- Liquid levels can be lower where gas-phase temperatures provide adequate protection.
- Look for condensed moisture or frost on the outer shell or rapid evaporation which indicates a vacuum loss. Transfer materials to another refrigerator as soon as possible.

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Cold Traps

Cold traps are used in instrumentation and other systems to prevent the introduction of liquids, vapors, or contaminants into the system. Single finger traps, U-traps, or other shaped lines are submerged in cryogenic liquids or slushes to provide a very low temperature surface on which the molecules condense. Cold traps also improve the achievable vacuum in systems by one or two orders of magnitude.

Improperly managed cold traps can impair accuracy, destroy instruments, and present a physical or health hazard. Many of the slush mixtures used in cold traps are toxic or explosive hazards and may not be indicated in the literature.

Cold traps exposed to atmospheric air may liquefy air resulting in an accumulation of liquid oxygen and nitrogen in the line. In the presence of organic materials this can result in a dangerous oxidation reaction. Also, if liquefied air is exposed to atmospheric pressure by opening a valve, the liquefied air will be pushed through the line by atmospheric pressure and when it contacts warmer plumbing, the liquid will rapidly expand to gas causing the gas to shoot through the line at nearly explosive velocities.

First Aid

Asphyxiation:

- If a person becomes dizzy move them to a well ventilated area immediately.
- If breathing has stopped apply artificial respiration or cardio pulmonary resuscitation (CPR) immediately.
- Call emergency services and keep them warm and calm.

Frozen Tissue:

- Restore tissue exposed to liquid cryogens to normal body temperature (98.6^{o}F) as rapidly as possible.
- Remove or loosen clothing that may restrict blood flow to the frozen tissue. Rapid warming can be achieved by using warm water at 108^{o}F. Under no circumstances should the temperature exceed 112^{o}F.
- Protect tissue from further damage or infection. Do not rub warming tissue before or after warming.
- Get medical attention.

References

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