CRYOGENIC LIQUID HANDLING STANDARD

Last updated: January 22, 2018

TABLE OF CONTENTS

1.0 PURPOSE

Cryogenic liquids can cause significant injury and property damage when handled improperly. Potential dangers include frostbite, explosions, and asphyxiation. This standard contains guidance on the controls required when using cryogenic liquids at the University of Waterloo. It provides information on:

- Required training for individuals using and individuals working in proximity to cryogenic liquids.
- Appropriate controls required when using, storing and handling these liquids.
- Generic emergency procedure for dealing with the accidental release of a cryogenic liquid.

2.0 SCOPE

This standard applies to the use of any cryogenic liquid on campus.

3.0 OPERATIONAL REQUIREMENTS

3.1 TRAINING FOR USERS OF CRYOGENS

Before an individual may use a cryogenic liquid, they must understand the hazards and risks associated with working with it and how to minimize and control these risks. Individuals must complete the following in order to work with and handle cryogenic materials:

- Cryogenic and Compressed Gas Safety training module – SO1030 (Online)
- Laboratory Safety training module – SO1010 (Online)
- Read and understand this standard
- Read and understand the MSDS/SDS for the cryogen being used

Each supervisor of an employee expected to work with a cryogen will provide hands-on training that contains:

- A description and a list of hazards associated with the equipment required
- A list of operating procedures
- A list of personal protective equipment (PPE) required and how to use it
- An emergency spill response and uncontrolled venting of cryogenic storage devices
- Information on reporting incidents

3.2 TRAINING: NON-USERS OF CRYOGEN LIQUIDS IN LABS CONTAINING CRYOGENS

Any individual not directly working with a cryogenic liquid, but working in a laboratory where compressed gases are used must complete the following training:

1. Laboratory Safety training module – SO1010 (Online)
2. Read and understand this standard
3. Training by the Principal Investigator (PI) on responding to the uncontrolled release of a cryogen (What to do if….)

4.0 IDENTIFYING HAZARDS AND RISKS

All cryogens are gases at room temperature. A gas has the added hazard of being an extremely cold liquid when condensed. Below is a list of the most common hazards.

- **Extreme cold:** These liquids are at temperatures of -90^{o}C or lower. Contact with these liquids or their vapours by a material or a person is dangerous. Human tissue will rapidly freeze, while materials normally pliable or ductile will become brittle, and will become more fragile when stressed.
    - **Frostbite:** Contact with a cryogen will instantly freeze bodily tissues. Eventually, as the tissues thaw, there is extreme pain. Some tissues may experience permanent damaged.
    - **Flesh tearing:** If bodily tissues touch another object frozen by a cryogen (normally a metallic object), the body will stick to that object. Removal of the body may cause flesh tearing.
    - **Material embrittlement and shrinkage:** Some materials become brittle and can fracture when contacted with extreme cold. Plastic, glass, rubber, and even carbon steel are examples of these materials. Some materials may also shrink more than their anticipated rate if contacted with a cryogen.
- **Oxygen deficiency (asphyxiation hazard)**
  Upon exit of their container, these liquids will expand more than 600 to 800 times their initial volume. The gases are heavier than air and therefore push out any air currently occupying a space so only the gases remain. For this reason, venting of storage and transfer dewars as well as overall room ventilation are key components of working with these materials.

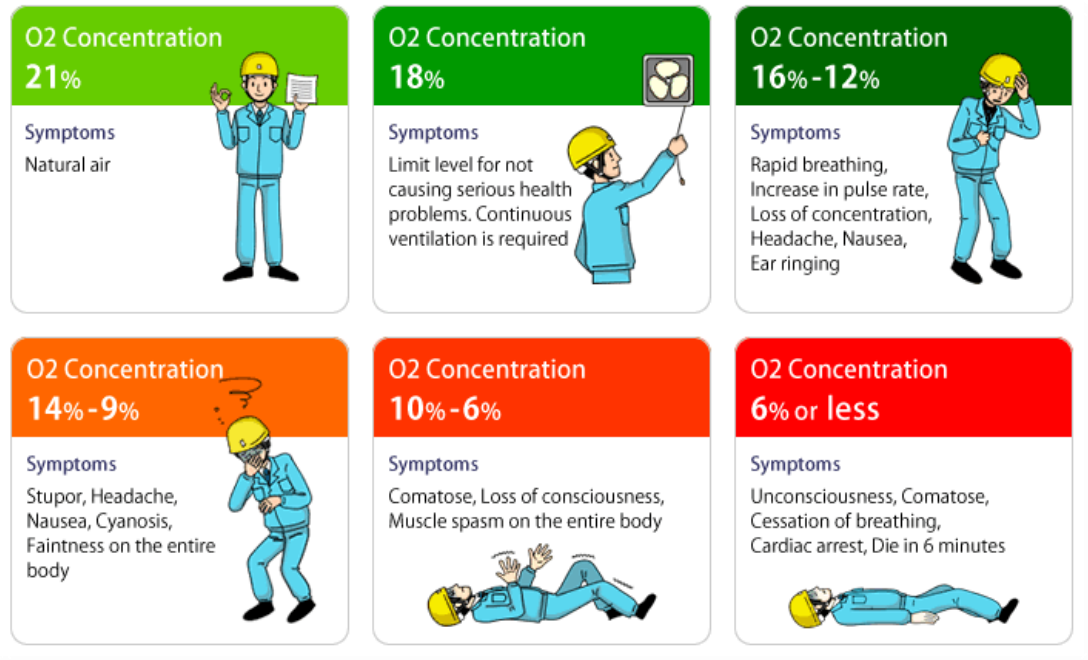


Figure 1: Symptoms of Oxygen Deprivation

- **Gas specific hazard:** Some cryogenic liquids also have specific hazard properties based on their chemical nature. For instance, in gaseous form, hydrogen is a flammable gas, carbon monoxide is flammable and toxic gas, and oxygen is an oxidizing gas. When released, these cryogenic liquids will retain their gaseous properties as they expand.
- **Boiling and splashing:** When a cryogen is added to a warm container or if a warm object is lowered into a container of a cryogen, the large temperature difference may cause the liquid to rapidly vapourize. Physically, this means the liquid will boil, splash and splatter, creating a cold contact hazard.
- **Pressurization:** Cryogens in storage devices are particularly susceptible to over-pressurization. This can occur in several ways:
    - **Ice plug formation:** Air can enter the storage device after the initial bleed off if the transfer valve remains open. If this occurs, moisture from the air can enter the device and freeze. Freezing occurs in the neck of the device creating an ice blockage that renders pressure relief valves inoperative.
    - **Sealing a pressure relief device:** If a pressure relief device is plugged, the pressure inside a cryogenic storage device will increase as the cylinder warms. If not remedied, the cylinder will eventually explode. Some pressure relief devices (PRD) come threaded to allow the user to attach vent pipes to the PRD and direct vent gas away from critical equipment and personnel. Do not use these to plug the device.

- **Ice build-up on critical or sensitive equipment:** Ice can build up around areas if they are uninsulated or if relief valves vent directly onto these areas. Ice buildup can potentially weaken or embrittle some materials, add weight to supports, ruin O-rings, and block relief valves or access to other critical valves.

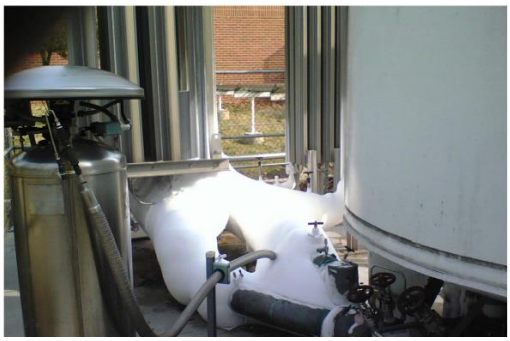


Figure 2: Image of ice build-up

- **Oxygen enrichment:** At temperatures less than 82 K (-191°C), metal surfaces will condense oxygen and form enriched air which may drip and form pools. In these liquefied pools of air, nitrogen will boil off first, leaving an oxygen-rich condensate on the surface. These surfaces can thus readily ignite.

4.1 HAZARD ASSESSMENT

Complete a hazard assessment before using a cryogenic liquid. The purpose of the assessment is to identify and control hazards likely to be present. Conduct a hazard assessment for cryogens using the following steps:

1. **Identify** the chemical nature of the specific cryogenic liquid you are using. Once released, the liquid will become a gas and retain its gaseous properties. The most commonly used cryogenic liquids at UWaterloo and their most relevant properties are in Table 1 below.

Table 1: Summary of the most common cryogens used at the University of Waterloo

Substance	Expansion Ration	Gas Classification	Links
Liquid Air	Similar to Nitrogen	Oxidizer	Not available
Nitrogen	1 to 694	Inert	**Guidance**
Helium	1 to 757	Inert	**Guidance**
Argon	1 to 847	Inert	**Guidance**
Hydrogen	1 to 851	Flammable	**Guidance**
Oxygen	1 to 860	Oxidizer	**Guidance**
Carbon Dioxide	1 to 845	Inert	**Guidance**
Carbon Monoxide	1 to 669	Toxic, flammable	**Guidance**
Liquified Natural Gas	1 to 621	Flammable	Not available

2. **Determine** the volumes of cryogen used, transferred, and stored. This data will help determine if adequate ventilation is available for the location of intended use. This **Cryogenic Calculator** can identify ventilation requirements. Contact the Safety Office for assistance.

3. **Obtain** appropriate PPE. This may include:
    - Face shield
    - Loose fitting insulated or leather gloves (loose fitting so they can be removed easily). Note – these gloves are not immersion resistant, and use tongs if immersing items into the cryogen.
    - Long pants without cuffs
    - Long sleeve shirts
    - Cryogenic aprons (recommended – especially for prolonged handling of cryogens)

    *More information on PPE later in this document.
4. **Inspect** all cryogenic storage devices and systems before and during use. Use PPE during inspections.

    - **Before use:**
        - Ensure pressure relief and rupture disks have clear, unobstructed paths, free of dirt, debris, rust and anything else.
        - Identify areas with rust, dents and cracks.
        - Check pressure gauges for cracks or signs of malfunction.
        - Ensure valves are tight with no apparent rust or frost buildup.
    - **During use (monthly):**
        - Ensure pressure relief valves and rupture disks are not blocked or plugged (visually check for dust, debris, and/or rust).
        - Identify areas with rust, dents and cracks on dewars and storage devices.
        - Check pressure gauges for cracks or signs of malfunction.
        - Check for sweat or frost on the underside of a container as this indicates a problem with the vacuum jacket; call the supplier or manufacturer for guidance.
        - Ensure storage devices that continuously vent are operating properly and call the supplier or manufacturer for guidance if they are not.

    Refer to Appendix 1 for specific guidance on troubleshooting problems with storage devices.

    Remember: Remove questionable system components from service!

5. **Minimize** the exposure of any cryogenic system to air by:
    - Keeping valves that lead to ambient air closed and only opening them when required.

- Purging transfer lines with a compatible inert before inserting it into a cold storage device.
- Using check valves or extended length tubs on vents normally open to air.

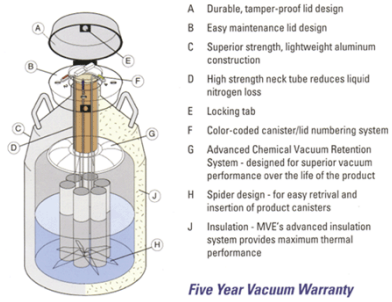
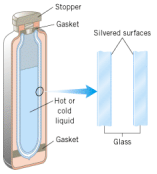
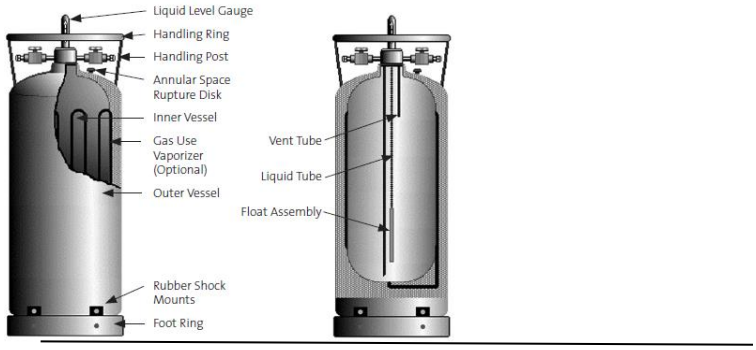
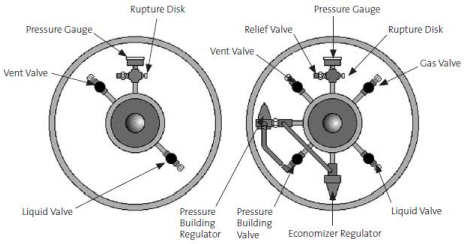
6. **Create** Standard Operating Procedures (SOP) that outline:
    - PPE required
    - How each process is performed (i.e. Lowering items into a cryostat).
    - How to set up the process:
        - Location of storage device
        - Where to direct vent pipes
        - Where to place drip pans
        - When and which lines should be insulated
    - What to do in case of continuously venting dewars, cryostats or other cryogenic storage devices
    - What to do in an emergency
    - What to do in case of a personal exposure to a cryogen
    - How to inspect the dewar
    - Responsibilities for inspections, transport and filling

Once the information above is gathered for the cryogen(s), all risks can be identified, and all controls can be verified.

4.2 CRYOGENIC STORAGE DEVICES

Cryogenic storage devices provide a safe method of maintaining a cryogen at its working temperature. The two main types of portable storage devices used at the University of Waterloo are the Dewar and the Cryogenic Liquid Cylinder. Table 2 describes both of these.

Table 2: Descriptions and images of Dewars and Cryogenic Containers

Dewars	Cryogenic Liquid Containers
Dewars are used primarily for 2 purposes: Storage and transport of cryogens Storage of materials in an ultra-cold environment	Cryogenic liquid containers are used for the storage and transport of medium to large volumes of cryogenic liquids.
Dewar  **Dewar Flask**  	**Side View**  **Top View** 

4.2.1 PERSONAL PROTECTIVE EQUIPMENT (PPE)

Whenever the handling or transferring of cryogenic fluids might result in exposure to the cold liquid, boil-off gas, or surface, wear the following PPE:

- Face shield
- Loose fitting thermally insulated gloves, or loose fitting leather gloves (gloves should be loose so they can be thrown off quickly in case of contact with the liquid as they only provide temporary protection – not immersion resistance
    - Gloves should be dry and grease free
- Long sleeved shirt, no cuffs
- Pants without cuffs (pants should not be tucked into boots and no short skirts)
- Closed toed shoes
- Insulated tongs rated for cryogenic use

Recommended clothing are items that are non-absorbent to keep spilt cryogens away from the skin. Some materials include leather, PVC, etc.

4.2.2 BEST PRACTICES FOR THE USE, HANDLING, AND STORAGE OF CRYOGENIC:

Dewar pre-use:

Visual inspections: The purpose is to identify rust, dents, cracks, and inappropriate frost buildup on the outside of the dewar.
Valve inspections: The purpose is to ensure valves are tightened securely, and there are no rust, or leaks apparent.
Pressure relief/Rupture disk inspection: determine if there is an unobstructed vent path, with no rust, frost, or debris buildup.

Figure 3: Cryogenic Liquid Container

Transfers:

- Use only fitted transfer tubes designed for the specific dewar used.
- Only fill dewars to 80% capacity (in temperatures above 30^{o}C fill capacity reduces to 60%).
- Immediately recap any container to avoid atmospheric moisture freezing in the cylinder.
- Transport dewars with hand carts.
- Stand clear of boiling and splashing liquids, and avoid the resulting cold vapours.
- Avoid touching uninsulated piping.

Lowering items into dewars:

- Lower items into dewars in a controlled and slow manner to avoid the formation of boiling and splashing liquid.
- Use tongs designed for contact with cryogens when lowering items into dewars.
- Do not lower warm items (above room temperature) into the dewars.

Storage:

- Store in well-ventilated areas only.
- Keep away from heat sources.
- Avoid contact with moisture.

When spilt on a surface, cryogenic liquids will spread quickly. Upon exposure, items and areas will cool rapidly. The vapours coming from the liquids are also extremely cold.

5.0 EMERGENCY RESPONSE GUIDELINES

All laboratories are required to have an emergency response plan for the hazardous materials they use, including cryogens. For cryogens, these plans should try to anticipate the type of release that could occur with the material in question. Determine the severity of the release by the following factors:

- Speed of release
- Gaseous properties of the materials in question
- Types of controls in place
- Amount of local and general exhaust in location

5.1 UNCONTROLLED RELEASE

If a cryogen releases in an uncontrolled manner, the user should be able to determine if shutting of the flow safely is an option by closing or sealing the rupture point. Depending on the speed of the release, the action would be to evacuate the localized area of release (laboratory) or evacuate the building. Pull the nearest fire alarm to evacuate the building if the release is rapid, or involves an explosion.

1. Barricade or seal of the local area of release (place signs and caution tape).
2. Call UW Police Services at extension 22222 and indicate what has happened, the location, and answer any questions they ask.
    - They will meet the fire department at the main entrance of the University and direct them to the release area.
3. Call Central Plant at extension 33793 and request the building be set to 100% fresh air.
4. Obtain MSDS/SDS and follow emergency release instructions unless the specific emergency response plan developed by the lab is more detailed and appropriate.

Once the area is evacuated and isolated, only trained Emergency Response Personnel with proper PPE and monitoring equipment are authorized to the enter the release area.

Appendix 2 contains other special precautions for specific cryogens. Before using the chemicals, use these to create specific emergency SOPs for the laboratory based on the chemicals used.

5.2 PERSONNEL EXPOSURE

People suffering from lack of oxygen should move to fresh air. If the victim is not breathing, administer artificial respiration. If breathing is difficult, administer oxygen. Obtain immediate medical attention. Self-contained breathing apparatus (SCBA) will prevent asphyxiation of rescue personnel.

For skin contact with cryogenic liquid nitrogen, remove any clothing that may restrict circulation to the frozen area. Do not rub frozen parts, as tissue damage may result. As soon as practical, place the affected area in a warm water bath that has a temperature of 105°F (40°C) or below. Never use dry heat. Call a physician as soon as possible.

Frozen tissue is painless and appears waxy with a possible yellow colour. It will become swollen, painful, and prone to infection when thawed. If the frozen part of the body thaws, cover the area with a dry, sterile dressing with a large bulky protective covering, pending medical care. In the case of a massive exposure, remove clothing while showering the victim with warm water. Call a physician immediately.

If the eyes are exposed to the extreme cold of the liquid nitrogen or its vapours, immediately warm the frostbite area with warm water not exceeding 105°F (40°C) and seek immediate medical attention.

APPENDIX 1: CRYOGENIC CONTAINER TROUBLESHOOTING GUIDE – REPRODUCED FROM AIR LIQUIDE SAFETY GRAM 27

Issue	Possible Cause	Recommended Activity
Gas vents intermittently through safety relief valve (7) when container is not in use.	Probably normal operation. Gas generated due to heat leak into cylinder causes head pressure to build.	Ensure inactive containers are stored in well-ventilated area. Rotate inventory.
Gas vents continuously through safety relief valve (7).	Possible relief valve failure or excessive heat leak.	Remove container or vent exhaust to a well-ventilated area. Relieve product through vent valve (4). Check to see if safety relief valve (7) is frozen open. Call supplier for assistance.
Gas vents during use through the safety valve (7).	Set point on regulators (3) or (8) exceeds safety relief valve setting.	Reduce set point on pressure building relief regulator (8).
Pressure in the container is low.	Leak from container.	Use appropriate leak detection fluid to check for leaks in connections. Examine container for signs of frost. If leaks on container itself, contact supplier.
	Pressure building valve (9) is not fully opened.	Open valve fully.
	Pressure building regulator (8) not set high enough.	Adjust to increase pressure.
	Gas withdrawal rate exceeds design capability of container. Pressure building regulator (8) may not be functioning properly.	Refer to 2 for system capabilities. Manifold multiple containers together if necessary.
	Incorrect container may have been ordered or delivered.	Contact suppler for assistance.
	Pressure building valve (9) is open.	Close the valve if frost is visible on the pressure building vaporizer (14) near the bottom of the tank.
Pressure in the container is too high.	Leak in or improper setting of pressure building regulator (8).	Reduce regulator setting to achieve desired pressure level. If pressure building vaporizer is frosted and the safety relief valve pressure setting is exceeded, call supplier to service regulator.
	Gas withdrawal rate is low.	Utilize and store in a well-ventilated area. Increase product withdrawal rate or bleed excess pressure through vent valve (4) into a well-ventilated area.
	Vacuum integrity failing.	If container walls covered with frost, contact supplier.
	Excessive product in container.	Vent or use product.
Pressure fails to change when pressure building valve (9) adjusted.	Problem with vaporizer coil. Pressure building valve (9) is stuck in closed position.	Call supplier. Call supplier.
Container wall covered with frost less than 8" from the bottom.	Pressure building vaporizer (14) in use to increase pressure.	If pressure building valve (9) is open, this is normal. If it is not, call supplier.
Container wall covered with frost to height of >10" from the bottom.	Gas withdrawal vaporizer (1) is in use.	Normal operation if gas withdrawal valve (11) is open. If not, call supplier.
Container top covered with frost.	High product use. Leak in fittings such as sight glass.	Normal operation. Call supplier.
Container has isolated spots of frost.	Container may have been damaged, compromising integrity of insulation.	Call supplier.
Container surface is uniformly covered with frost.	Vacuum integrity compromised.	If accompanied by high rate of product venting through safety relief valve (7), or high rate of pressure increase, call supplier.
Gaseous product is too cold.	Product withdrawal rate is greater than the design delivery rate of the container.	Reduce product withdrawal rate or manifold multiple containers together to achieve desired flow rate.

APPENDIX 2: SAFETY CONSIDERATIONS FOR THE RELEASE OF SPECIFIC CRYOGENS

SPECIAL INERT GAS PRECAUTIONS

When handling inert cryogenic liquids, it is vital to recognize the potential for asphyxiation. Because cryogenic liquids have high expansion ratios, air can be displaced quickly. It is recommended to use oxygen monitors whenever handling cryogenic liquids in enclosed areas. People should not be in atmospheres containing less than 19.5% oxygen without supplied air. Liquid helium has the potential to solidify air, which can block pressure-relief devices and other container openings. This can result in pressure buildup that may rupture the container.

SPECIAL OXYGEN PRECAUTIONS

There can be no open flames in any areas where liquid oxygen is being stored or handled. Do not permit liquid oxygen or oxygen-enriched air to contact organic materials or flammable or combustible substances of any kind. Some of the organic materials that can react violently with oxygen when ignited by a spark or even a mechanical shock are oil, grease, asphalt, kerosene, cloth, tar, and dirt that may contain oil or grease. If liquid oxygen spills on asphalt or if other surfaces become contaminated with combustibles, do not walk on or roll equipment over the spill area. After all frost or fog has disappeared, keep sources of ignition away for 30 minutes. If clothing is splashed or soaked with liquid oxygen, or if the clothing is exposed to high oxygen concentrations, remove it immediately and air it out for at least an hour. Personnel should stay in a well-ventilated area and avoid any source of ignition until their clothing is completely free of any excess oxygen. Clothing saturated with oxygen is readily ignitable and will burn vigorously.

SPECIAL HYDROGEN PRECAUTIONS

There should not be an ignition of any kind in areas where storing or handling liquid hydrogen. Properly ground all major pieces of equipment. All electrical equipment and wiring should be in accordance with National Fire Protection Association Pamphlet 50B and/or National Electrical Code, Article 500. Vent boil-off gas from closed liquid hydrogen containers used or stored inside buildings to a safe location. Liquid hydrogen should not be poured from one container to another or transferred in an atmosphere of air. If this occurs, the oxygen in the air will condense in the liquid hydrogen, presenting a possible explosion hazard. Liquid hydrogen also has the potential to solidify air, which can block safety relief devices and other openings and may lead to container rupturing. Do not use dewars or other containers made of glass for liquid hydrogen service. Breakage creates the possibility of an explosion, which is too hazardous to risk. Make every effort to avoid spills, regardless of the rate of ventilation, as it is impossible to avoid creating a flammable vapour cloud.