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Requirements
for

Safe Handling of Cryogenic Liquids

REVISION

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1. PURPOSE

1.1 This procedure has been written to provide information governing the hazards associated with cryogenic materials, guidelines on the requirements for handling, transporting and using cryogenic fluids and to prevent injuries and accidents that involve the use of cryogenic fluids.

1.2 Cryogenic materials are very cold substances (gases, solids and liquids that exist at or below -100° F) that are used in a wide variety of processes. By definition, cryogenic liquids have boiling points ranging from -78.5°C (-109°F) for carbon dioxide to -269.9°C (-454°F) for helium. Common liquid cryogens used at the CNSE facility include liquid nitrogen (N2), liquid helium (He), and solid carbon dioxide (dry ice) although there are many others including liquid oxygen (O2), liquid hydrogen (H2) and liquid argon (Ar).

2. SCOPE

2.1 To provide guidance on the storage, use and handling of cryogenic liquids at the College of NanoScale Science and Engineering (CNSE) facility. Partially full containers having residual cryogenic liquids and shall be considered as full for the purposes of the controls required.

3. DEFINITIONS

3.1 Cryogenic liquids - are liquids that exist between -66°C and -266°C.

3.2 Compressed gas cylinder - any cylinder specifically designed to contain gases under pressure of greater than one atmosphere, and having the capability of dispensing the gas by the means of a control valve mechanism to assure the safe and proper use of the gas at a point of operation.

3.3 Dewar - An insulated container used especially to store liquefied gases, having a double wall with a vacuum between the walls and silvered surfaces facing the vacuum. Small hand carried Dewars range in size from 1L capacity to 20L, while large Dewars that are equipped with their own lockable wheels for ease of transport, can range in size from 20L to 100L.

4. PHYSICAL PROPERTIES AND HAZARDS OF CRYOGENIC LIQUIDS

4.1 The table below lists the physical properties of common liquid cryogens.

	Boiling Point (K)	Liquid-to-gas Expansion Ratio (ft^3)	Gas Specific Density	Critical Temperature (K)	Critical Pressure (atm)	Liquid Density (g/l)	Explosive/ fire danger
Air	--	--	1.0	--	--	--	No
Argon	87.3	860	1.39	150.9	48.3	1402	No
Carbon Dioxide	194.7	790	1.70	304.2	72.8	1560	No
Helium	4.2	780	0.14	5.2	2.2	125	No
Hydrogen	20.3	865	0.07	33.0	12.8	71	Yes
Nitrogen	77.3	710	0.97	126.3	33.5	808	No
Oxygen	90.2	875	1.11	154.8	50.1	1410	Yes
R-12	243.4	294	4.35	385	40.6	1487	No

4.2 Physiological Hazards - Severe cold "burns" or frostbite may be inflicted if the human body comes in contact with cryogenic fluids, boiled-off vapor, or surfaces cooled by cryogenic fluids. The evolution of large volumes of gases associated with evaporation of cryogenic liquid spills can result in asphyxiation. For instance, nitrogen expands approximately 700 times in volume, going from liquid to gas at ambient temperature. Asphyxiation and chemical toxicity are hazards encountered when entering a cryogenic vessel that has been used to store cryogenic liquids if proper ventilation/purging techniques are not employed.

4.3 Material Hazards - The selection of materials calls for consideration of the effects of low temperatures on the properties of those materials. Some materials become brittle at low temperatures. Brittle fracture can occur very rapidly resulting in almost instantaneous failure. Low temperature equipment can also fail due to thermal stresses caused by differential thermal contraction of the materials. Over pressurization of cryogenic equipment can occur due to the phase change from liquid to gas if not vented properly. All cryogenic fluids produce large volumes of gas when they vaporize.

4.4 Flammability and Explosion Hazards - Fire or explosion may result from the escaping of flammable gases such as hydrogen, carbon monoxide, or methane. Escaping liquid oxygen, while not a flammable gas by itself, can combine with combustible materials and cause spontaneous combustion. Oxygen clings to clothing and cloth items and presents an acute fire hazard for approximately one-half hour after exposure.

4.5 High Pressure Gas Hazards - Potential hazards exist in highly compressed gases because of the stored energy. In cryogenic systems high pressures are obtained by gas compression during refrigeration, by pumping of liquids to high pressures followed by rapid evaporation, and by confinement of cryogenic fluids with subsequent evaporation. If this

confined fluid is suddenly released through a rupture or break in a line, a significant thrust may be experienced.

5. RESPONSIBILITIES

5.1 Managers/Supervisors/Professors are responsible for ensuring that this policy is implemented. Dissemination of this information to the relevant persons including CNSE faculty, staff and students, and ensuring that suitable training, maintenance and inspection procedures are set up and documented will help ensure safety in cryogenic material use.

5.2 Personnel who are responsible for any cryogenic equipment must coordinate a risk assessment with the Environmental, Health and Safety (EHS) department prior to the commencement or operation of such equipment. Additional safety reviews must follow any system modification to ensure that no potentially hazardous condition has been overlooked or created and that updated operational and safety procedures remain adequate.

5.3 Key elements of ensuring safety are:

5.3.1 Risk assessment of each storage and dispensing area.

5.3.2 Risk assessments of activities involving cryogenic materials.

5.3.3 Training users and keeping records of this training.

5.3.4 Providing the necessary equipment and personal protective equipment (PPE).

5.3.5 Written procedures and emergency procedures for the use and handling of cryogenic materials.

5.3.6 Consulting with the EHS department when large facilities or significant changes are being considered.

5.3.7 Carrying out periodic inspections to confirm that procedures are being followed.

5.3.8 Ensuring that there is adequate security to prevent unauthorized access.

5.3.9 Personnel working with cryogenic fluids must follow the guidelines for use, handling, transportation and storage listed in this procedure.

6. RISK ASSESSMENT

6.1 An initial risk assessment must be performed in which the potential depletion in oxygen concentration from the largest foreseeable spillage must be calculated for all facilities where cryogenic materials are stored or handled. The calculation is shown below. Where this could result in an oxygen concentration below 18%, corrective actions must be implemented to mitigate the potential.

6.2 Possible actions include limiting the maximum quantity of cryogenic fluid handled so that oxygen depletion cannot arise, moving the operation to a larger room, providing mechanical ventilation with indicators that it is operating and installing oxygen alarms.

6.3 Where the risk assessment shows that mechanical ventilation and oxygen alarms are needed, the EHS department must be consulted before any action is taken. Risk assessments, written operating procedures and training are needed to cover the full range of hazards associated with storage and use of cryogenic materials.

6.4 The Manager/Supervisor/Professor of the area is responsible for the development of workplace specific safety information related to the use and storage of cryogenic liquids.

7. HAZARDS ASSOCIATED WITH CRYOGENIC MATERIALS

7.1 Oxygen Deficiency and Asphyxiation - The most significant risk of cryogenic liquids is death by asphyxiation where a spill or leakage depletes the atmospheric oxygen. If the oxygen concentration falls below 18% adverse effects will occur resulting in loss of mental alertness and performance combined with distortion of judgment. In atmospheres containing less than 10% oxygen, death by asphyxiation is rapid: just two breaths of oxygen-free air kills.

7.1.1 For example, oxygen depletion resulting from a spill of 50 liters in a room 5m x 10m x 3m is calculated below and can be determined using the equation: Where V_0 is 0.209 (V_r - V_g) (for cryogenic liquids other than oxygen) V_r is the volume of the room, and V_g is the maximum gas release upon the expansion of the cryogenic liquid 100 X 0.209(150 - (0.05 m3 X 682))/150m3 = 0.209 X 115.9 X 100/150 = 16.2% [To calculate the oxygen concentration when oxygen is the cryogenic liquid, V_o in the formula becomes 0.209(V_r –V_g) + V_g].

7.1.2 If someone is seen unconscious in a cryogenic handling or storage area it is likely that they are already dead and there is a serious risk to rescuers

of being asphyxiated; unless they are wearing self-contained or air-line-supplied breathing apparatus, and are trained in entry procedures for confined spaces. In such circumstances, the first actions should be to call the Emergency number 78600 or (518) 437-8600, and evacuate the immediate area, opening doors and windows, if safe to do so, on the way out.

7.2 Cold Burns, Frostbite and Hypothermia - Contact of the skin with cryogenic liquids (or even cold gas) can cause severe cryogenic burns; the tissue damage that results is similar to that caused by frost bite or thermal burns. While the cold itself can reduce the feeling of pain, the subsequent thawing of tissue can cause intense pain.

7.2.1 Contact with non-insulated parts, equipment or vessels containing cryogenic liquids can produce similar damage. Unprotected parts of the skin may stick to low-temperature surfaces and flesh may be torn upon removal.

7.2.2 Inhalation of cold vapor can cause damage to the lungs and may trigger an asthma attack in susceptible individuals.

7.2.3 Hypothermia is a risk due to the low temperatures arising from the proximity of cryogenic liquids. Risk is dependent upon the length of exposure, the atmospheric temperature and the individual; those exposed for prolonged periods should be warmly clothed.

7.3 Oxygen Enrichment - Although not flammable, oxygen when present in higher concentrations can significantly increase the chance of fire or an explosion. The boiling point of oxygen is above those of nitrogen and helium. In closed systems (such as cold traps cooled with liquid nitrogen) these liquids can cause oxygen to condense on their surface (resulting in a bluish liquid on the surface). This can lead to; the ignition of normally non-combustible materials, and the flammability limits of flammable gases and vapors being widened. Oil and grease may spontaneously ignite and, as such, should not be used where oxygen enrichment may occur.

7.4 Pressurization and Explosion - Cryogenic liquids that vaporize with a volume change ratio of 700-900 can cause violent changes in pressure, particularly if this occurs in a confined space. This in turn can result in an explosion. Vent systems must be in place to allow gas to escape from confined spaces. Pressurization can occur due to the following:

7.4.1 Ice forming on the venting tube, plugging it and preventing gas release.

7.4.2 Damaged equipment resulting in cryogenic fluids leaking into small areas. Upon vaporization the cryogenic liquid vaporizes and causes pressure build up.

7.4.3 Loss of vacuum inside a cryostat or Dewar.

7.4.4 If a liquid helium-cooled superconducting magnet "quenches" (changes spontaneously from a superconducting state to a normal state).

7.4.5 Liquid nitrogen having permeated through sealed cryotubes containing samples which then return to room temperature.

7.4.6 Direct contact of the cryogenic liquid with water in a tube results in rapid vaporization of the cryogenic liquid and can cause the tube to explode.

7.5 Damage to Equipment - The very cold temperatures of cryogenic liquids can damage equipment and materials, which can result in danger to personnel. Examples of damage include the following:

7.5.1 Spilled liquid nitrogen can crack tiles and damage flooring such as vinyl.

7.5.2 Rubber tubing may become brittle and crack during use.

7.5.3 Condensation of water around electrical cables may result in an electrical shock hazard.

7.6 Flammable Gas - Hydrogen is extremely flammable and should be treated with extreme caution. Areas of use should be restricted, clearly marked, and well ventilated. No naked flames, electrical ignition sources, sources of static electricity, or potentially combustible materials should be allowed within the restricted area, as any of these could result in an explosion if gas has escaped. Liquid hydrogen can condense and solidify air resulting in an explosion hazard. For this reason closed hydrogen systems should be used to prevent backflow of air.

8. GENERAL SAFETY PRACTICES

8.1 Personnel Safety

A face shield, safety glasses, loose fitting insulating protective gloves and apron shall be worn at all times when transferring, pouring, dispensing, and with normal handling of cryogenic fluids. Shirt sleeves will be rolled down and buttoned over glove cuffs, or an equivalent protection such as a lab coat will be worn in order to prevent liquid from spraying or spilling inside gloves. Trousers without cuffs will be worn.

8.2 Safety Practices

8.2.1 Cryogenic fluids must be handled and stored only in containers and systems specifically designed for these products and in accordance with applicable standards, procedures, or proven safe practices.

8.2.2 Transfer operations involving open cryogenic containers, such as Dewars, must be conducted slowly to minimize boiling and splashing of the cryogenic fluid. Transfer of cryogenic fluids from open containers must occur below chest level of the person pouring liquid.

8.2.3 Such operations shall be conducted only in well ventilated areas to prevent the possible gas or vapor accumulation, which may produce an oxygen-deficient atmosphere and lead to asphyxiation. The volumetric expansion ratio between liquid and atmospheric nitrogen is approximately 700 to 1.

8.2.4 Equipment and systems designed for the storage, transfer, and dispensing of cryogenic fluids shall be constructed of materials compatible with the products being handled and the temperatures encountered.

8.2.5 All cryogenic systems, including piping, must be equipped with pressure-relief devices to prevent excessive pressure build-up. Pressure-reliefs must be directed to a safe location. It should be noted that two closed valves in a line form a closed system. The vacuum insulation jacket should also be protected by an over-pressure device if the service is below 77° Kelvin. In the event a pressure-relief device fails, do not attempt to remove the blockage; instead call the emergency number 78600 or (518) 437-8600 immediately.

8.2.6 If liquid nitrogen or helium traps are used to remove condensable gas impurities from a vacuum system that may be closed off by valves, the condensed gases will be released when the trap warms up. Adequate means for relieving the resultant build-up of pressure must be provided.

9. REFILLING DEWARS IN LABORATORIES

9.1 Make sure that there is adequate ventilation. Open the door if you are in a small room (10' x 10').

9.2 Remove watches, rings and other metal jewelry on hands and wrists before handling cryogenic liquids.

9.3 Wear the required PPE as identified in the PPE Standard EHS-00010. In general the following PPE as the minimum is required:

- Safety glasses.
- Faceshield.
- Cryogenic gloves.

- Cryogenic apron.
- Lab coat with sleeves pulled over cuffs of cryogenic gloves.
- Full length cuffless pants that extend over shoe tops.
- Closed-toed shoes that are impervious to liquids, such as leather, or covered with liquid proof shoe covers/spats.

9.4 Only use Dewars rated for the cryogen being transferred.

9.4.1 Never use a Dewar that does not have a pressure relief valve or pressure venting lid or stopper.

9.4.2 Use pressure venting lids or stoppers supplied by the Dewar's manufacturer.

9.4.3 Never use Dewars with makeshift or homemade lids/stoppers.

9.4.4 Glass Dewars must be taped solidly around the outside. The plastic mesh which comes with some small thermos bottles primarily provides some protection for the Dewar, but does not necessarily protect against glass shards resulting from implosion.

9.4.5 Dewars larger than 20 Liters must be transported and poured by two people.

9.4.6 Never use a funnel during filling, due to the possibility of the cryogenic liquid overfilling and propelling upward.

9.4.7 Ensure the receiving vessel is dry.

9.4.8 The receiving vessel must be raised so the delivery tube is immediately above the mouth of the vessel (i.e. the cryogenic liquid should never be allowed to fall through air to reach the receiving vessel). Use a table, cart or other mechanical means to position the vessel in the proper location. Never hold the vessel with unprotected hands while filling.

9.4.9 To reduce thermal shock, first cool the receiving vessel by dispensing a small amount of cryogenic fluid then, continue the dispensing process. Dispensing should be conducted slowly to minimize splashing, spilling and thermal shock to the receiving vessel.

9.4.10 Do not move or bend the fill tube during filling.

9.4.11 Stay out of the vapor pathway during dispensing.

9.4.12 Do not leave a filling operation unattended.

9.4.13 Only use approved materials with cryogens. Unapproved materials (such as plastic, Styrofoam, rubber, wrought iron, hollow tubes, and carbon steel) will become brittle and shatter, or in the case of hollow tubes become over pressurized.

9.4.14 Periodically inspect equipment; remove ice and frost blockages from openings to prevent over pressurization.

9.4.15 Do not tamper with pressure relief valves. Report any leaks or improperly set relief valves to the manufacturer. It is normal for large Dewars to periodically vent resulting in a loud hissing noise, however if you hear a whistling noise coming from a large Dewar this is an indication that it is empty.

9.4.16 Equipment should be kept clean without the use of corrosive cleaning materials that could damage the metal jacket.

9.4.17 When manually pouring liquid into a smaller Dewar, ensure that the secondary container is secured, pour slowly to prevent excess splashing, do not overfill, and use a phase separator, if available, to control the vapor path while pouring.

10. TRANSPORT OF CRYOGENIC LIQUIDS

Special precautions must be taken to prevent a spill while transporting cryogens, in addition to minimizing exposures from liquids and vapors. The high liquid to vapor expansion ratio could rapidly displace all oxygen in a room and result in asphyxiation. Implement the following procedures to minimize exposures:

10.1 Transport within the laboratory or lab building.

- Wear all required PPE; safety glasses and steel-toed shoes.
- Use handcarts equipped with brakes for large Dewars and cylinders.
- Never transport an open container of a cryogenic liquid.

10.2 Transport outside the laboratory or lab building.

10.2.1 Plan the route of transport. **AVOID USING AN ELEVATOR.** In event of an elevator failure or spill, the space may quickly undergo oxygen displacement. If this is not avoidable, send your buddy to the receiving floor. Then load the Dewar or cylinder. Remain on the sending floor while you send the Dewar or cylinder to the receiving floor unmanned. After your buddy unloads the Dewar or cylinder, join him/her for the rest of the

transport. If the transport by elevator takes place over multiple floors, clearly label the Dewar or cylinder with a warning to anyone who may want to use the elevator between the sending and receiving floors to wait until the transport process is complete.

10.2.2 Always use care when handling equipment. Damage to Dewars could result in the loss of vacuum and increased evaporation. Transport of helium Dewars requires extra care because they are fragile.

10.2.3 When at all possible, do not hand-carry cryogenic liquids. For larger Dewars use a stable wheeled base designed for the Dewar transport. Check to ensure stability before commencing transport.

10.2.4 When carrying a Dewar, make sure it is the only item you are carrying. Hold the Dewar as far away from the face as possible. Be on the lookout for other people who may run into you or bump you.

10.2.5 Large mobile Dewars used for transport should be equipped with a braking mechanism. Do not use feet to brake. Steel-toed boots are recommended.

10.2.6 Take care to avoid crushing hands or fingers between the vessel or cart and walls or door frames.

10.2.7 If there is any risk of tipping, a cart should be used. Wheeled trolleys may not be used if the vessel must pass over elevator thresholds or other slots/crevasses wider than 25% of the wheel width.

11. STORAGE OF CRYOGENIC LIQUIDS

A cryogenic liquid storage unit left open to the atmosphere, or catastrophic failure of a storage unit, could create an oxygen deficient atmosphere. Follow these procedures to reduce the likelihood of this occurrence:

11.1 Glass Dewars must have an exterior coating/cover to minimize projectiles in the event of an explosion. Newer Dewars may have a plastic mesh over the exterior for this purpose. Older Dewars must be replaced.

11.2 Only store Dewars in well-ventilated rooms with a minimum of six air changes per hour.

11.3 If the ventilation rate is unknown, contact the Facilities department to evaluate the affected area.

11.4 The EHS department may recommend the installation of oxygen detection systems and alarms for cryogenic liquid storage areas depending on location, ventilation, and quantity of material stored.

11.5 Do not store cryogenic liquids with corrosive or flammable chemicals.

11.6 Storage units should be placed so that vents and openings are oriented away from personnel and lab equipment.

11.7 Bulk cryogenic liquid dispensing areas within buildings must be well ventilated, and be equipped with continuous oxygen monitoring equipment.

11.8 Storage of cryogenic liquid Dewars in hallways, unventilated closets, environmental rooms, and stairwells is prohibited.

11.9 No more than one backup Dewar is allowed per piece of equipment using cryogenic liquids in research labs. Additional Dewars must be stored in areas designed for such storage. Contact the EHS department to evaluate potential storage locations.

12. EMERGENCY PROCEDURES AND FIRST AID

12.1 Liquid Nitrogen (LN2) is the most commonly used cryogenic liquid. Oxygen depletion resulting from nitrogen gas may occur rapidly with no warning properties. A person entering an oxygen deficient environment may become disoriented and unable to respond properly. Nitrogen gas is odorless, colorless, tasteless, and inert. The failure of a large Dewar could spill 180 L of LN2 which in gas form will completely displace all oxygen in a 21x21x10 ft room. A much smaller spill in the same room could still create a safety hazard. Simply reducing the oxygen content in a room below 19.5 % is considered an oxygen deficient environment. Implement the following procedures to minimize the risk of asphyxiation:

12.1.1 If ventilation in the room is less than six air changes per hour, contact the EHS department for advice about installing an oxygen level detection alarm.

12.1.2 If a spill occurs (<1 liter), immediately evacuate the area. With adequate ventilation, it may be appropriate to return to the area after thirty minutes. For large spills (>1 liter) contact the ERT at 78600 or (518) 437-8600 immediately as the area may need to be monitored for oxygen levels before it can be determined when it is safe to re-enter.

12.1.3 If experiencing symptoms such as lightheadedness, dizziness, or confusion, immediately get fresh air and receive medical attention.

12.1.4 If an employee becomes unconscious in a cryogenic liquid storage area call the ERT at 78600 or (518) 437-8600 immediately as they should only be retrieved by personnel using proper PPE (such as a Self Contained Breathing Apparatus). The ERT are the only personnel on site that are

trained to use this equipment. Over fifty percent of deaths associated with asphyxiation in confined spaces occur to would-be rescuers.

12.1.5 Once personnel have been removed to fresh air, the ERT will provide rescue breathing or CPR until paramedics arrive. In the event that skin or the eyes come into contact with cryogenic gases or liquid, follow first aid procedures, then immediately seek medical attention.

12.1.6 Immediately remove any clothing that has been contaminated. In the event of clothing contamination with oxygen, hydrogen, or carbon monoxide, it is important to remove clothing, evacuate personnel from the facility, and keep away from ignition sources.

12.1.7 Flush or soak the area with warm water (no greater than 105ºF).

12.1.8 Do not apply dry heat or rub damaged flesh or eyes.

12.1.9 Employees should notify their supervisor of injuries and complete an Injury and Illness Report Form EHS-00026-F1.

13. SPILLS AND DISPOSAL

13.1 Minor spill (< 1 liter)

13.1.1 Allow liquid to evaporate, ensuring adequate ventilation.

13.1.2 Following return to room temperature, inspect area where spillage has occurred.

13.1.3 If there is any damage to the floors, benches or walls, report it to Facilities and EHS departments.

13.1.4 If any equipment has been damaged following the spillage, inform the supervisor of the area.

13.2 Major release (> 1 liter)

13.2.1 Shut off all sources of ignition.

13.2.2 Evacuate area of all personnel.

13.2.3 Inform EHS department and the supervisor of the area.

13.2.4 DO NOT return to the area until it has been declared safe by EHS department.

13.3 Disposal Care needs to be taken when disposing of cryogenic liquids.

13.3.1 DO NOT pour cryogenic liquids down the sink - they will crack waste pipes causing potentially dangerous leaks.

13.3.2 DO NOT store cryogenic substances or allow them to vaporize in enclosed areas, including: fridges, cold rooms, sealed rooms and basements.

13.3.3 DO ensure that the area in which the cryogenic liquid is left to vaporize is well ventilated.

14. TRAINING REQUIREMENTS

14.1 OSHA's Hazard Communication Standard (29 CFR part 1910.1200) is designed to ensure that the hazards of all chemicals produced or imported are evaluated and that information concerning their hazards is transmitted to employers and employees.

14.2 Training should be given in all aspects of the use and handling of cryogenic materials. A combination of on the job skills, instructions and information covering the following areas provides a minimum standard to which all users must be trained. Topics to be covered in Cryogenic handling training include:

- Understanding of the Material Safety Data Sheet (MSDS), the risks involved and where to obtain information
- Understanding the risks and effects of oxygen depleted atmospheres
- Conducting a risk assessment
- Use of PPE
- Handling cryogenic materials
- Moving containers of cryogenic materials (>1 liter)
- Emergency procedures
- Spillage procedures, and if necessary
- Manual handling of larger storage vessels
- Dispensing bulk quantities (> 1 liter)

14.3 Training Proficiency – The effectiveness of training shall be determined via results of proficiency exams administered to each individual completing the training session.

14.4 Training records shall be located with the EHS manager. Such records shall include the nature of the training, content, the date and length in hours, instructor(s), participants, and training proficiency exam results.

14.5 Training shall be conducted on initial assignment and annually.

15. RECORDS

15.1 All risk assessment records, training records, installation and maintenance records shall be kept on file in the EHS office.