University of South Australia

WHS GUIDLINE

SAFE USE OF LIQUID NITROGEN (AND OTHER CRYOGENICS)

1. PURPOSE AND SCOPE

Cryogens such as liquid nitrogen and liquid helium that affect the content of oxygen in air can result in life threatening asphyxia which can be sudden (immediate) or gradual (over a few minutes or hours). Either situation can result in death. There is also potential for anyone attempting a rescue to be exposed to low levels of oxygen and becoming a subsequent casualty. Contact with liquids, vapour or gas at cryogenic temperatures can produce an effect on the skin similar to a burn. The severity depends upon the temperature of the liquid and the exposure and can result in frostbite.

A cryogenic liquid includes liquid nitrogen (LN2), liquid argon (Lar), liquid helium (LHe), liquid hydrogen (LH2), liquid oxygen (LO2), among others. Whilst not strictly a cryogen, for the purposes of this guideline dry ice (solid carbon dioxide) will also be included as it is also routinely used a cooling agent.

Liquid nitrogen and other cryogens are widely used throughout the university for various tasks. This guideline provides advice on how to ensure that hazards from the storage, transportation and handling of liquid nitrogen and other cryogens are well managed and risk of injury or illness to personnel is eliminated or mitigated. The information in this guideline relates to liquid nitrogen and other cryogens that are stored in either fixed or portable vessels.

2. DEFINITIONS

Asphyxia is the condition that arises when the blood is deprived of an adequate supply of oxygen.

Asphyxiant is a gas or vapour which has no toxic properties but which, when present in sufficient concentrations, excludes oxygen, and can lead to asphyxia and/or death.

Cryogens or cryogenic liquid is a liquid having a normal boiling point below minus 90ºC at atmospheric pressure (101 kPa).

Dewar is a portable, double-walled container, which is normally open-necked, free-venting, and non-pressurised, and is used for storing cryogenic liquids.

Dry Ice (solid carbon dioxide) does not have a liquid state at normal atmospheric pressure and sublimates directly from the solid state to the gas state at minus78 ºC.

Manifest is a written summary of the hazardous chemicals used, handled, or stored.

Pressurised vessel is designed, constructed, and protected in accordance with AS 1210 or AS 2030 and has a water capacity of at least 50L (bulk pressurised storage vessels have a water capacity greater than 500L) and does not freely vent, but has pressure relief valves and vents.

Safety Data Sheet (SDS) contains information on the identity of a product and any hazardous ingredients, potential health effects, toxicological properties, physical hazards, safe use, handling and storage, emergency procedures, and disposal requirements specific to the chemical.

Shall indicates that a statement is mandatory.

Should indicates that a statement is a recommendation.

Venting is the discharge of gas vapours out of a cryogenic storage container.

3. IDENTIFIED RISKS AND CONTROLS

Cryogens can be used in a variety of ways and for differing purposes. Liquid nitrogen and other cryogens are commonly utilised for specialty chilling and freezing applications, including cryogenic tempering of metals. Another use of cryogens is for fuels in rockets, with liquid hydrogen a widely used example. Cryogenic liquids and solids have an extremely low temperature. When cryogens transition from liquid to gas, or solid state directly to gas for dry ice, large volumes of gas are produced. Liquid methane, liquid hydrogen, and liquid oxygen present additional hazards that liquid nitrogen and liquid argon do not. The following table summarises the physical properties of common cryogens:

Cryogen	Boiling Point (ºC)	Gas Density (g/L)	Liquid to Gas Expansion Ratio	Type of Gas
Argon	- 186	1.63	1 : 840	Inert
Carbon Dioxide (Dry Ice)	- 78	1.45	1 : 845	Inert
Helium	- 269	0.16	1 : 750	Inert
Hydrogen	- 253	0.08	1 : 850	Flammable
Nitrogen	- 196	2.25	1 : 695	Inert
Oxygen	- 183	1.4	1 : 860	Oxidising
Methane	- 161	0.72	1 : 630	Flammable
Neon	- 246	0.90	1 : 1440	Inert

3.1 Hazards and Risks

The hazards arising from the use of liquid nitrogen and other cryogens are:

- Asphyxiation in oxygen deficient atmospheres: when liquid nitrogen and other cryogens boil, gases are produced, that can displace oxygen from the air. Even small amounts of cryogens can rapidly expand into large volumes of gas. This can result in an oxygen-deficient atmosphere, particularly if vented into a closed space, and possibly cause asphyxia.
- Cold burns, frostbite, and hypothermia: due to their extremely low temperatures, cryogens and their associated cold vapours and gases, can rapidly freeze human tissue producing effects on the skin similar to a thermal burn. Cold vapour or gas may cause frostbite with prolonged or severe exposure of unprotected body parts. Unprotected skin can stick to metal or other uninsulated conductive material that is cooled by cryogenic substances can stick to the skin and flesh may be torn on removal. Prolonged breathing of extremely cold air may damage lungs and transient exposure can produce discomfort in breathing and may provoke an asthma attack in susceptible individuals.
- Over-pressurisation: liquid nitrogen and other cryogens exhibit large volume expansion ratios which can cause rapid pressure changes and pose a high risk of explosion. For example, boiling of liquid nitrogen within a closed system increases pressure rapidly as gaseous nitrogen occupies up to 682 times the volume of liquid nitrogen and this will lead to pressure build up in the system.
- Combustion and explosion hazard: cryogens with a boiling point lower than liquid oxygen, such a nitrogen and helium, can condense oxygen from the atmosphere. If the atmosphere is enriched with oxygen, this higher oxygen content increases the combustibility of many materials, creating potentially explosive conditions.

- Thermal stress/ embrittlement: materials frozen due to contact with cryogens may change characteristics which may cause the material to become brittle or even fracture under stress. Damage can also be caused due to large, rapid changes in temperature.
- Health hazards: gases released from cryogens can cause specific adverse health effects and brief exposure to small volumes of cryogens that would not affect the skin can damage the eyes. Refer to the chemical SDS for information about the health hazards for the specific cryogenic liquid.

3.2 Controlling Risks

If the use of liquid nitrogen and other cryogens is necessary, the risks must be assessed and adequately controlled. It is important to consider the task being performed and the quantities of cryogens used to select the appropriate control measures. A Chemical Process Risk Assessment must be undertaken, and control measures implemented, monitored, and adjusted as needed. Information on the location and quantities stored must be included in the chemical manifest in Chemwatch.

The risk of asphyxia must be assessed wherever liquid nitrogen or other cryogens are used or stored, taking into account the volume present in relation to the room volume, the likelihood of leakage or spillage, the normal evaporative losses that occur and any ventilation arrangements. Refer to Appendix 1 for further information on calculating the risk.

Areas where liquid nitrogen or other cryogens are stored or used shall be ventilated, to prevent the accumulation of gas or vapour which could evaporate from the liquid, and/or disperse the gas or vapour evaporating from any liquid spill, without reducing the oxygen content of the surrounding air below 18%. Equipment must also be kept clean to prevent contact with oil, grease and combustible materials which can be hazardous as liquid nitrogen can absorb atmospheric oxygen thus becoming oxygen enriched and increasing risk in the event of fire.

Regardless of oxygen concentration, the University requires that rooms containing more than 50 litres of a cryogenic liquid (whether in pressurised vessels or dewars) shall be fitted with a low oxygen alarm.

3.2.1 Storage, Handling and Use of Dry Ice

Dry ice converts to carbon dioxide gas at minus 78 ºC and therefore is not strictly defined as a cryogen. However dry ice is routinely used as a cooling agent in laboratories and during transport of biological materials and many of the same identified risks apply. Appropriate controls must be implemented to eliminate or minimise the risks associated with the use, handling and storage of dry ice.

Dry ice must not be placed in a sealed container at temperatures above its boiling point. As dry ice warms it reverts to its gaseous state, causing expansion and any container that does not allow for the release of gas means a build-up of pressure, can cause the container to rupture, or explode.

Do not use or store dry ice in confined areas or rooms without ventilation including cold-rooms, as carbon dioxide in high concentrations may cause asphyxiation. Whilst many factors can affect the rate at which dry ice sublimates from solid state to gaseous state including ambient temperature and humidity and the number of times the container is opened and closed, an ultra-low temperature (minus 80 ºC) freezer is deemed appropriate for the storage of dry ice.

The control measures detailed below for other cryogens should also be applied to the management of dry ice.

3.2.2 Purchasing

Completion of the Chemical Process Risk Assessment (using the online system) is required prior to purchase of cryogens to enable planning for the management of any risks. Only equipment designed specifically for cryogens shall be purchased for the storage or handling of liquid nitrogen and other cryogens.

3.2.3 Access and Training

Only authorised and trained personnel shall have access to bulk storage areas and must not provide entry to unauthorised persons. Entry points to storage areas must be kept clear to allow for emergency access or egress, and clear access to fire-fighting equipment and housekeeping equipment located nearby.

All personnel involved with the transport, storage, handling and disposal of liquid nitrogen or other cryogens must complete the online Liquid Nitrogen training course and practical training, and be deemed competent with the use of pressurised vessel/s and/or dewars and relevant safe work procedures, prior to use.

3.2.4 Bulk Storage

The quantity of cryogens permitted to be stored in an area depends on the volume and ventilation of the area. Consideration shall also be given to the location of any potentially hazardous processes in the vicinity which might jeopardise the integrity of the storage, or on which the storage might impact. The following requirements shall also be met:

- Site (preferably outdoors) must be accessible to the cryogen's supplier for filling and maintenance and allow for adequate venting of gas when liquid nitrogen or other cryogens are being decanted.
- An area shall be designated for safe filling of vessels from a delivery vehicle ensuring the area has a level surface, and a quick exit can be made in the event of an emergency.
- Placards are displayed indicating WARNING RESTRICTED AREA, AUTHORISED PERSONNEL ONLY.
- If stored internally, an alarm shall be fitted to eliminate the risk of a person entering a room and to alert any personnel within the area of an insufficient oxygen to sustain life and interlocked with the door access (if further information is required contact the University Chemical Safety Officer or the Safety & Wellbeing team).
- Adequate venting must be provided where liquid nitrogen or other cryogens are stored or used, and venting shall not occur into an area where people may congregate or otherwise inadvertently be exposed to venting gas.
- Pressure relief valves must be installed in piping between isolatable points.
- Adequate lighting must be provided in and around storage areas to ensure personnel are able to read labels and signs as needed.
- Water must be readily available in the vicinity of the storage.
- A plan must be in place to combat an emergency, developed in liaison with the Campus Facilities Manager and shared with all personnel with access to the bulk storage area. The plan should include action to be taken in the event of a first aid event, spill, explosion, leak, or other emergency consistent with the Emergency Management procedure.

Bulk storage vessels and their associated equipment shall be inspected by a competent person every 4 years (external) and for vacuum-insulated vessels, a vacuum reading taken every 6 years and pneumatically tested for leak-tightness every 12 years. Pressure relief valves must be overhauled or replaced every 5 years.

3.2.5 Storage in Pressurised Vessels

Liquid nitrogen and other cryogens shall only be stored in pressurised vessels specifically designed to contain cryogens. Areas with immediate ventilation to outdoors (i.e., siting the vessel against an external wall with permanent openings equivalent in size to the width of the vessel and of a height from floor level to the vessel fill point) are preferred. Where outdoor ventilation cannot be met, the space in which the vessel is kept shall be ventilated sufficiently to ensure that the oxygen content in the atmosphere will not be reduced below 18% in the event of total evaporation of entire vessel contents.

Pressurised vessels and their associated equipment (i.e., pressure relief valve) shall be inspected quarterly to detect signs of deterioration, damage or evidence that suggests damage or deterioration may exist.

3.2.6 Storage in Dewars

Only dewars that have been specially designed for cryogenic liquids shall be used. Domestic flasks must not be used. Special care shall be taken to avoid bumping and jarring when using and handling the dewars. Inspect dewars for damage prior to use. Any cap supplied with the dewar shall be fitted when the contents of the dewar are not in use and sufficiently loose-fitting to prevent pressure build-up.

Dewars shall be clearly marked to show the liquid for which the vessel or equipment is designed and used. Marking shall be in accordance with the Hazardous Chemical Labelling Guideline.

3.2.7 Dispensing / Decanting

The method of decanting liquid from a pressure vessel or dewar will depend on the design. Small dewars may be tilted to pour liquid from the neck. Pressurised vessels use the gas pressure to force the liquid from the dewar. All personnel must be trained on how to use the dewar or pressurised vessel before use. Always check containers for signs of wear or damage prior to use and do not use if any defects are detected. During the process of dispensing/ decanting, access to the area shall be controlled with no access for unauthorised persons. Do not fill containers to more than 80% of capacity. Precautions must be taken to prevent spillage.

3.2.8 Transportation

Only containers and trolleys that have been specifically designed for transportation shall be used. When using a trolley for external transportation consideration of the conditions (quality of the path and/or road surface and current weather) shall be made. When transporting in small dewars (4L or less), tape the cap down loosely to prevent it from falling off whilst still allowing ventilation. Larger volumes of cryogens (greater than 4L) should be transported using dewars on wheels with pressure relief valves or pressure venting lids.

If containers of liquid nitrogen are to be transported by vehicle, a dry shipper should be used. Transportation between campuses or delivery to campus should be undertaken by an appropriately licensed dangerous goods carrier. Under no circumstances shall cryogen liquids be transported in an enclosed vehicle (i.e., cryogenic liquids may be transported in a utility tray).

People should not travel in lifts with liquid nitrogen or other cryogenic liquids to eliminate any risk of asphyxiation in the event of a spill. Lifts should be locked out to ensure no person inadvertently enters the lift during transit with liquid nitrogen or other cryogenic liquids and a clearly documented procedure must be in place. Where this is not practicable, the maximum volume of cryogenic liquid that can be transported in a lift with people, shall be determined in consultation with the University Chemical Safety Officer and clearly displayed.

3.2.9 Handling / Use

Avoid direct contact with cryogens or objects frozen with a cryogen. Use tongs and dippers to withdraw or immerse objects and always place materials slowly into cryogens. Rapid splashing and boiling of cryogens can occur when dispensing into a warm container (e.g., at room temperature) or when inserting warm objects into the cryogenic liquid.

When cryogens are used in cold traps attached to vacuum pumps, these traps must be emptied immediately after use. Where processes that generate large amounts of gas such as food freezing, freezing of tissue samples or cells are conducted indoors, the gas produced shall be vented by mechanical means into the atmosphere away from areas where people work or congregate.

3.2.10 Disposal

Never dispose of cryogens down the sink. Small volumes shall be vented in a fume cupboard. Larger volumes should only be vented outdoors. Venting shall not take place into trenches, pits, drains or confined spaces, or near people.

3.2.11 Personal Protective Equipment

Personal protective equipment (PPE) is only designed to protect from incidental contact with a cryogenic liquid. However, appropriate PPE shall always be worn when handling cryogens. PPE shall cover skin and eyes in a manner that allows for easy removal in the event of a spill and must not hamper the user's ability to handle the cryogens safely.

- Hand protection: wear thermally insulated gloves specifically designed for handling cryogens or smooth leather welding type gloves. Gloves should be loose fitting to allow for easy removal in the vent liquid is spilled inside the glove and the sleeves of the laboratory coat should be pulled down over the glove to prevent any liquid from entering the gloves. Cryogenic gloves are designed for indirect or splash protection only, they are not designed to protect against immersion into cryogenic liquids.
- Eye/ face protection: when filling dewars or transferring cryogenic liquids from one container to another, a full-face shield must be worn. For any other handling of cryogens or materials in cryogenic liquids, safety glasses must be worn.
- Body protection: Laboratory coats or coveralls must be worn to minimise the potential for skin contact. When filling dewars or transferring cryogenic liquids from one container to another, long pants must be worn (on the outside of footwear). Enclosed footwear, preferably made from non-absorbent materials, must be worn and arms and legs should not be exposed whilst handling cryogens.

3.2.12 First Aid

All people who use liquid nitrogen or other cryogens must be advised of emergency and first aid procedures in the event of an emergency. First aid officers shall be educated in the first aid measures required in the event of an injury involving a cryogen and trained in the emergency plan for bulk storage areas, as required. In no circumstances is it considered safe to enter an oxygen-deprived environment for the purpose of patient rescue without a self-contained breathing apparatus.

3.2.13 Emergency Management

Any emergency shutdown systems shall be tested on a regular basis. If a plug of frozen material forms beneath the lowest vent in a dewar or pressurised vessel containing cryogenic liquid, it is unlikely that the vessel will be able to withstand the pressure that can build up. The formation of a frozen plug can be indicated by:

- A disconnected transfer line or pipe that is known to have been connected;
- An inability to insert the transfer line;
- A lack of detectable boil-off; or,
- Ice formation around the neck of the dewar or pressurised vessel.

The dewar or pressure vessel should be disconnected, if possible, and personnel evacuated from the area. Any attempt to remove the plug shall only be made by emergency services personnel.

Liquid oxygen and liquified nitrous oxide pose special hazards due to their vigorous support of combustion and shall be separated from flammable liquids and gases and all ignition sources by at least 5 metres.

4. UNIVERSITY DOCUMENTS / FORMS

For further advice on managing risks in university workplaces, including procedures, guidance, forms, and training courses, please visit the Safety & Wellbeing website.
Safety & Wellbeing website

- Managing Workplace Health and Safety Risks
- Safe Management of Chemicals
- Chemical Process Risk Assessment system (MyOSH CRAs)
- WHS12 – Chemical Process Risk Assessment and Control (For use by undergraduate students only)

Facilities Management Unit, University Emergency Management
Online Hazard/Incident Reporting & Investigation System

5. REFERENCES

SafeWork SA Resources—WHS legislation and Approved Codes of Practice:

- Work Health and Safety Act 2012
- Work Health and Safety Regulations 2012
- How to Manage Work Health and Safety Risks
- Managing Risks of Hazardous Chemicals in the Workplace

Government of South Australia, Dangerous Substances Act 1979
National Transport Commission, Australian Code for the Transport of Dangerous Goods by Road or Rail ('ADG Code')

Australian Standards online

- AS 1894 -1997, *The storage and handling of non-flammable cryogenic and refrigerated liquids*.
- AS 2030.4 – 1985, *The verification, filling, inspection, testing and maintenance of cylinders for storage and transport of compressed gases, Part 4: Welded cylinders – Insulated.*
- AS 1319:1994, *Safety signs for the occupational environment.*

(Note: This may not be a complete list of applicable Australian Standards)

APPENDIX 1: OXYGEN DEPLETION CALCULATIONS

To determine oxygen concentrations after normal evaporative and filling losses, the following calculations can be used.

Step 1: Normal evaporative losses.

(a) $$N_E = \frac{2 \times 682 \times (D_N \times D_E)}{24 \times 1000}$$

(b) $$A_D = \frac{N_E}{R_v \times R_A}$$

(c) $$O_D = 0.21 \times 100 \times A_D$$

Where:

- N_E is the nitrogen evaporation rate (in m^3h^{-1}).
- 2 safety factor to allow for the deteriation of the dewar's insulation.
- 682 expansion factor for liquid nitrogen to gaseous nitrogen.
- D_N is the number of dewars.
- D_E is the evaporation rate from the dewar (L/day) (obtained from the supplier of the dewar).
- A_D is the fractional reduction in the air concentration due to the conversion of liquid nitrogen to gaseous nitrogen.
- R_V is the volume of the room (m^3).
- R_A is the number of room air changes per hour.

Step 2: Filling losses.

(a) $$O_V = 0.21 \times [R_V - (0.1 \times D_V \times 682 \times 0.001)]$$

(b) $$O_C = \frac{100 \times O_V}{R_V}$$

Where:

- O_V is the volume of oxygen in the room (m^3).
- D_V is the volume of the dewars (L).
- O_C is the oxygen concentration (%)

Step 3: Total oxygen concentration in the laboratory.

$$O_T = O_C - O_D$$

Where:

- O_T is the total oxygen concentration in the room (%)

(Adapted from University of Oxford Policy Statement S4/03.
http:// www.admin.ox.ac.uk/safety/s403a1.shtml accessed 6 Jan 2005)