Chemical Risk Management Protocol

Safe Methods of Use (SMOU)

Cryogenic Materials

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Acknowledgement

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1 Purpose

This Safe Method of Use (SMOU) applies to principal investigators (PIs), laboratory managers, designated laboratory person (DLPs), and all staff and students who direct or participate in the use of cryogenic materials, at the University of Auckland.

2 Disclaimer

The Safety Data Sheet (SDS) should be consulted for specific information about the chemical you will be using. The Gold FFX SDS Database is available on the Library database. Instructions on how to source this information can be found on the Health, Safety and Wellbeing Databases website:

https://www.auckland.ac.nz/en/health-safety-wellbeing/health-safety-topics/laboratory-safety/chemical-safety/databases.html

Please read this SMOU in conjunction with the Chemical Risk Management Guidelines.

Note: 'Shall' denotes a mandatory requirement and 'should' denotes a recommendation.

PART A: LIQUID NITROGEN AND OTHER CRYOGENIC LIQUIDS

3 Hazards of Cryogenic Liquids

There are two major hazards associated with cryogenic liquids such as liquid nitrogen (-195.8 °C) and liquid helium (-268.93 °C); asphyxiation (suffocation due to lack of oxygen) and cryogenic burns/frostbite.

3.1 Asphyxiation

Cryogenic liquids will expand many times their original volume when they convert to gas at room temperature. One litre of liquid nitrogen produces approximately 680 litres of nitrogen gas.

If vented into a closed space, cryogenic liquids such as helium, argon and nitrogen will displace oxygen when they become gaseous and have the potential to create oxygen deficient environments. Because of the nature of the gases involved, the victim will have no warning that they are in or entering an oxygen-deficient environment.

It is important to note that asphyxia will occur without warning, as the human body reacts to increased blood carbon dioxide not lack of oxygen.

Asphyxia – Effect of O_2 Concentration

O_2 (Vol %)	Effects and Symptoms
18-21	**No discernible symptoms** can be detected by the individual. A risk assessment must be undertaken to understand the causes and determine whether it is safe to continue working.
11-18	Reduction of physical and intellectual performance **without the sufferer being aware**.
8-11	Possibility of fainting within a few minutes without prior warning. **Risk of death below 11%.**
6-8	Fainting occurs after a short time. **Resuscitation possible** if carried out immediately
0-6	Fainting almost immediate. **Brain damage**, even if rescued.

***WARNING**: The situation is hazardous as soon as the oxygen concentration inhaledis less than 18 %.*

3.2 Burns

Cryogenic liquids are, by definition, extremely cold. Contact between cryogenic liquids and exposed skin can produce a painful cryogenic burn. A splash of cryogenic liquid to the eye can cause loss of vision.

Emergency Treatment for Burns

- Raise the burnt area to room temperature using tepid water.
- Do not use warm water.
- Do not remove clothing around burn as it may lift frostbitten skin.

3.3 Other Hazards Associated With Cryogenic Liquids

3.3.1 Transporting Liquid Nitrogen in Lifts

1. Liquid nitrogen ***shall*** travel unaccompanied in the lift.
2. If a general service lift is being used it is important that this transport of liquid nitrogen takes place at a time when the lifts are not being used (i.e. outside of peak times).
3. If the lift cannot be commandeered by key control, then is advisable that two people work together to transport liquid nitrogen via the lift. One person should be stationed on the relevant floor to receive the liquid nitrogen when the lift arrives. The second person places the approved liquid nitrogen container in the lift, places a warning sign (if not already present in the lift) immediately behind the lift door so it will bar entry to the lift, and then selects the floor/level and exits the lift. The person on the receiving floor removes the liquid nitrogen and the sign when it arrives.
4. Liquid Nitrogen must not be carried up and down stairwells.

3.3.2 Pressure buildup

Boiling of liquefied gases within a closed system increases pressure. Users must make certain that cryogenic liquids are never contained in a closed system. Cold fingers and similar devices have exploded when either an ice dam is formed within the apparatus or when users create a closed system by shutting off all valves. Users should also tape exposed glass parts to minimise the hazard of flying glass shards in the event of an explosion.

3.3.3 Oxygen enrichment

Liquid nitrogen and liquid helium may fractionally distil air, causing liquid oxygen to collect in the cryogenic container. It can be identified by its light blue appearance. Liquid oxygen increases the combustibility of many materials, creating potentially explosive conditions. It must not be allowed to make contact with flammable or organic materials, including grease.

3.3.4 Embrittlement

Do not dispose of cryogenic liquids down the drain. Ordinary materials such as metal or polyvinylchoride (PVC) piping in laboratory sinks may not be able to withstand cryogenic temperatures.

Allow cryogenic liquids to evaporate in a fume hood or other well-ventilated area. Materials exposed to cryogenic temperatures for long periods or materials that have undergone periodic warming and freezing must be examined regularly for cracks and warping.

3.3.5 Cryotube Explosions

Cryotubes used to contain samples stored under liquid nitrogen may explode without warning when warmed. Tube explosions are caused by liquid nitrogen entering the tube through minute cracks and then expanding rapidly as the tube thaws. Cryotubes may be thawed behind shields or in fume hoods where the glass sash can provide shielding. When thawing cryotubes in the open, take the following protective steps:

- Wear a face shield, or at least safety goggles, whenever handling cryogenic liquids.
- Wear cryogenic gloves.

4 If something goes wrong

STOP, HAVE A MOMENT, THINK THEN ACT.

NEVER enter a room that may be oxygen-deficient, unless you are wearing self-contained breathing apparatus.

4.1 Spill or Leak

- **Large spill** or leak from a large tank: Evacuate the area, inform others not to go near the area, and call 111 and Security (966)
- **Minor spills**: increase ventilation if possible, leave the room for a short period if deemed necessary.

4.2 Cold Burn

Quick contact of liquid nitrogen on bare skin is generally not harmful. Prolonged contact can cause severe cold burns and frostbite to set in quickly. Move the exposed person to a warm area, remove clothing or jewellery, but not if frozen to skin.

- If liquid nitrogen has soaked through clothes, apply tepid water to the clothes before taking them off.
- If skin is stuck to a cold metal surface, do not try to pull it away. Instead flush with cold water.
- Rinse the affected area generously in tepid water for 10 to 15 minutes.
- Seek medical attention if required.

NEVER rinse in hot water

NEVER warm the affected area with dry heat

NEVER rub cold burnt or frostbite skin

5 Safe Storage of Cryogenic Liquids

Containers of cryogenic liquid must <u>never</u> be stored in small enclosed rooms.

- Liquid nitrogen, helium and argon *must never* be stored or used in basement area or pits where gas can accumulate and develop an oxygen-deficient atmosphere.
- Make sure to provide adequate venting when working with cryogenic liquids in a closed system or enclosed space.
- Cylinders and Dewars should not be filled to more than 80% of capacity, since expansion of gases during the warming may cause excessive pressure buildup.
- The Dewars should be stored close to the egress point.

Minimum Room Volumes for Storage of Containers of Liquid Nitrogen

The following minimum room sizes in Table 1 have been calculated to assist you select the correct location in which to place liquid nitrogen containers. Note that the room volume calculations are based on oxygen concentration not falling below 18% in the event of a 'worst case scenario' involving loss of all the liquid nitrogen in the container.

If it is impracticable to move the liquid nitrogen container (i.e., the container is attached or is an integral part of an item of equipment) the room must have an oxygen alarm.

Corridors are often continuous around the building so, all other considerations aside, they are the most likely places to have the required volumes in which to store larger volumes of liquid nitrogen.

Please refer to Appendix 1 for details of how these sizes have been calculated.

Table 1: Minimum room sizes required per volume of liquid nitrogen stored

Volume of Liquid Nitrogen (litres)	Minimum room size (m2) – assuming a 3-metre room height
10	18
25	45
30	54
40	72
50	90

5.1 Oxygen Alarms

Some areas with significant quantities of liquid nitrogen have oxygen alarms. These have a cartridge sensor which needs to be replaced every 24 months. The sensor should be calibrated every 12 months to compensate for measurement drift. In the event of cartridge failure, the unit will alarm (i.e., the instrument will 'fail safe').

6 Safe use of cryogenic liquids

6.1 PPE

The following shall be worn when pouring cryogenic liquids.

- Face shield
- Loose fitting Thermal Mittens or Cryogenic Gloves (that can be easily shaken off)
- Closed Shoes or boots
- If pouring cryogenic liquids ensure pants material is not tucked into shoes

6.2 Filling of dewars

- Ensure the main door is open when filling a liquid nitrogen storage dewar. In the event of a spill, the nitrogen generated will equilibrate with larger volumes in corridors and is less likely to displace oxygen to dangerously low levels.
- Never fill a cylinder behind closed doors.

PART B: SAFE USE AND TRANSPORTATION OF DRY ICE

7 What is dry ice?

Dry ice is a solid form of frozen carbon dioxide (CO_2) which sublimes into a gas state at -78.5°C. It is classed as a cryogenic material due to its low temperature, a class that includes liquefied nitrogen -196°C and helium -269°C among others. Dry ice is predominantly used as a temporary refrigerant as CO_2 has a lower temperature and has no liquid state like ice water. Other uses include fog machines, ice cream and cocktail making to blast cleaning. It can be supplied in the form of pellets, slices or blocks.

8 Hazards of dry ice

8.1 Frostbite and cold burns

Severe skin damage can occur quickly when dry ice or items cooled by dry ice are in contact with the skin for a prolonged time. This can cause cold burns and potentially frostbite leading to permanent skin damage. Contact with eyes, while rare can cause serious injury.

8.2 Asphyxiation

Dry ice will sublimate ([change from solid state directly to a gas state) at any temperature above -78.5°C releasing potentially substantial volumes of CO_2. 5kg of dry ice will produce 2.7m^3 of gas. Wetting of dry ice rapidly increases the rate of sublimation as this quickly raises the temperature. The gas given off by dry ice is non-flammable, odourless in small quantities and colourless. Normal air is 0.035% CO_2, 0.5% can become dangerous. This can cause headaches, difficulty breathing and in high concentrations loss of consciousness and death. Pregnant and asthmatic people will show symptoms of oxygen deficiency more quickly and should exercise further caution.

8.3 Explosion in over-pressurisation of vessel

Due to the sublimation properties, dry ice that is stored in a closed container can become pressurised due to the large volumes of CO_2 gas given off, even by a small amount of dry ice. Sealing a container with dry ice may cause it to violently explode or rupture if unable to escape.

9 Safe use of dry ice

9.1 Personal Protective Equipment [PPE]

Gloves – When handling dry ice appropriate thermal gloves must be worn. The gloves should be loose fitting to allow for rapid removal if required. Never handle dry ice with bare hands. Latex or nitrile can freeze and adhere to the skin and make removal very difficult.

Lab coat or suitable apron – When handling dry ice a lab coat of suitable length and fully buttoned up must be worn to avoid any pellets of dry ice making contact with skin e.g. On bare legs

Eye protection – When handing dry ice eye protection must be worn. This can either be safety glasses with side protection or a face shield.

Foot wear – Closed footwear must be worn when handling dry ice. Sandals or open toed shoes must not be worn under any circumstances as a pellet could get lodged between toes.

Note:- Carbon dioxide gas cannot be removed from the air by N95/N100 respirators or by PAPR's [Powered Aired Purifying Respirators]

All PPE should be carefully inspected for faults or defects prior to each use. Any damaged PPE should be taken out of service and not used.

9.2 Safe use

Before

Wear correct PPE listed above and beware of metallic jewellery, watch straps etc., that can quickly spread cold from contact with dry ice.

Have an appropriate container for disposal or storage of dry ice after use. This should be of a suitable size and construction *See next sections, Storage and Disposal*.

During

Use tongs or scoops as much as practicable when handling dry ice.

Perform all operations in a well-ventilated area and avoid inhalation or working closely with dry ice.

After

Leave the work area clean and ensure that all dry ice is collected in the original or appropriate container for storage or disposal.

10 Storage of dry ice

A suitable container for small amounts of dry ice is a polystyrene box (chilly bin) with a loose fitting lid that is not air tight, "breathable" but still insulated.

For larger amounts it is recommended to use a dry ice chest which is a more insulated construction container with low temperature lid seals where build-up of pressure is self-releasing. This allows for the dry ice to be stored in a safe manner for longer periods.

NEVER store in a gas tight sealed container that will not vent, such as a metal flask, glass bottle or plastic tub.

Bulk storage of dry ice should be avoided where possible. If deemed necessary a specific risk assessment should be performed; refer to this article for suggested control measures.[1]

NEVER store dry ice in fridges or freezers including ultra-low temperature freezers [ULTs]. This will cause the dry ice to sublimate faster due to the higher temperature of the fridge or freezer. Tightly sealed containers will allow for sufficient gas to build up and potentially explode.

Confined spaces or areas with little or no ventilation can result in a build-up of carbon dioxide.

NEVER store dry ice in walk-in cold rooms, cupboards, fridges, freezers or ULTs. Ensure any storage in corridors does not present a hazard to evacuation paths. *Refer to Section 12 Transport regarding safe ways to transport dry ice.*

11 Disposal

Allow the unused dry ice to sublimate at room temperature in a well-ventilated area for several days. *E.g. fume cupboard with correct air flow.*

NEVER submerge in water, as this will produce large quantities of CO_2 gas, increasing the risk of asphyxiation.

NEVER pour down sinks or drains, as this can damage the integrity of the plumbing.

NEVER dispose of in general or medi-waste rubbish bags.

12 Transporting dry ice

Always transport dry ice in an appropriate breathable container with a loose-fitting lid.

12.1 Transport around the building including lifts

Avoid transporting dry ice through heavily populated areas of the building or if unavoidable transport at a quieter time.

Dry ice **shall** travel unaccompanied in lifts, unless a thorough risk assessment deems a specific use case acceptable, considering:

- Size and ventilation of the specific lift, including whether ventilation continues during a power cut
- Maximum number of occupants to be allowed in the lift, and how to ensure no-one else enters (e.g. use a priority key, or a chain and sign across the lift entrance)
- Amount of dry ice to be carried
- Establishing a system where another person outside the lift is made aware when dry ice is being transported in an occupied lift

12.1.1 Best practice for transport in lifts

1. If a general service lift is being used it is important that this transport of dry ice takes place at a time when the lifts are not being used (i.e. outside of peak times).

2. If the lift cannot be commandeered by key control, then is advisable that two people work together to transport dry ice via the lift. One person should be stationed on the relevant floor to receive the dry ice when the lift arrives. The second person places the approved dry ice container in the lift, places a warning sign (if not already present in the lift) immediately behind the lift door so it will bar entry to the lift, and then selects the floor/level and exits the lift. The person on the receiving floor removes the dry ice and the sign when it arrives.

12.2 Transporting dry ice outside the building

- Never carry dry ice on public transport or taxis
- Use of a chemical courier is strongly recommended. Dry ice must not be transported within the cab of a car due to risk of oxygen displacement. If in a car boot, dry ice should only be transported for less than 1 hour, as the gas may start to penetrate the cab. It is preferable to use a Ute with a self-contained tray compartment instead.

All chemical transport/courier requests should begin with filling out the "Courier request form New Zealand Mail" form at the bottom of this page:

https://www.staff.auckland.ac.nz/en/central-services/finance-andpurchasing/strategic-procurement/strategic-suppliers/mail-and-couriers.html

UniLogistics will determine the most suitable courier to be used and will provide advice on packaging requirements.

13 If something goes wrong

STOP, HAVE A MOMENT, THINK THEN ACT.

Carbon dioxide gas is heavier than air. This gas will accumulate in low areas until it had equilibrated with the air. A small spill of dry ice on the floor can be carefully managed by collecting it with tongs or gloved hands.

Larger spills may require immediate evacuation and increasing the rooms ventilation, by fully opening the fume hood sash and opening windows/doors. Don't try to clean it up as this involves putting your face near the floor, where CO_2 gas will accumulate. Contact the lab manager and complete an online incident form.

13.1 First aid

Inhalation

If working around dry ice and you feel yourself becoming dizzy, headachey or having difficulty breathing move yourself away from the dry ice into an open well-ventilated area.

If inhalation of cold vapours has occurred the exposed person may be suffering from frostbite of tissue in their throat and lungs, but also asphyxia. Seek medical attention.

If unconscious, remove from area, but only if safe to do so. Self-contained breathing apparatus [SCBA] maybe required. Seek medical attention.

Skin contact

Quick contact of dry ice with the skin may cause a cold stinging feeling but is generally not harmful. Prolonged contact can cause severe cold burns and frostbite to set in quickly. Move the exposed person to a warm area, remove clothing or jewellery, but not if frozen to skin.

Rinse the affected area generously in tepid water for 10 to 15 minutes.

Seek medical attention if required.

NEVER rinse in hot water

NEVER warm the affected area with dry heat

NEVER rub cold burnt or frostbite skin

Eye contact

While rare, if dry ice has contacted the eye, using an eyewash station and holding open the eyelids flush the eye for several minutes.

Seek medical attention.

Ingestion

While rare, if the person is conscious, immediately drink room temperature tap water.

NEVER give anything by mouth to an unconscious person.

Seek medical attention

14 References

1. Park, B. J.; Vanderwal, C. D., Lessons Learned: Asphyxiation Hazard Associated with Dry Ice. *ACS Chemical Health & Safety* **2023,** *30* (3), 120-123.

Appendix 1. Basis of Calculations

The room size calculations are taken from a formula derived from British Compressed Gas Association Code of Practice 30 and working on the basis that oxygen concentration must not fall below 18% in a 'worst case scenario'.

Filling and spillage together

The 'worst case' scenario, where the entire contents of a dewar are lost to the room immediately after filling, equivalent to 110% of vessel contents to allow for the 10% filling losses prior to spillage:

$$V_o = 0.21 \left[V_R - \left[\frac{1.1 * V_D * f_g}{1000} \right] \right]$$

where:

1.1	=	110% volume loss during filling and spillage
V_R	=	room volume, m^3
V_D	=	dewar capacity, litres
f_g	=	gas factor. This is 683 for nitrogen. (Nitrogen gas takes up 683 times the volume of nitrogen liquid, ie one litre of liquid nitrogen creates 683 litres of gaseous nitrogen.)
0.21	=	The normal concentration of oxygen in air, 21%
*	=	multiply

Note Risk assessment must assume the worst case scenario of spillage after filling.

https://www.oxigraf.com/technical-support/

Vo derived from this equation is then used to calculate the percentage of oxygen after the event.

$$Cox = \frac{100 * Vo}{V_R} = \text{resulting oxygen concentration \%}$$

where:

V_O	=	the volume of oxygen, m^3
V_R	=	the room volume, m^3
*	=	multiply