USC UNIVERSITY OF SOUTHERN CALIFORNIA

STANDARD OPEARTING PROCEDURE FOR CRYOGENS

USC University of Southern California

DPS emergency number 213-740-4321

NATURE OF HAZARD

Cryogens are substances of low boiling point, below −150 °C, −153 °C, or −180 °C (123 K, 120 K, or 93 K, respectively) depending on the definition chosen, and which are liquid by virtue of being at low temperature. In a laboratory setting, cryogenic liquids are commonly held in insulated containers and kept cold only by their heat of evaporation, which means they continually boil away at a rate proportional to the heat flux flowing into the container.

Dry ice is frozen carbon dioxide. At atmospheric pressure, it sublimes to gas at −78.5 °C (194.7 K); it does not pass through the liquid phase unless the pressure is much higher. Although the temperature of dry ice is considerably above the range commonly considered cryogenic, the hazards are similar to other cryogens.

Liquid cryogen boiling points at atmospheric pressure are as follows: Helium 4.2 K; neon 27.1 K; nitrogen 77.3 K; air 79-82 K (boiling range, since it is a mixture); argon 87.3 K; oxygen 90.2 K.

Vacuum-insulated Dewar vessels are usually used for storage. Open-neck Dewars store liquid at atmospheric pressure; the opening is usually covered by a loose-fitting cap which excludes contaminants, but allows free escape of gas. Pressurized Dewars are closed vessels fitted with a pressure-relief valve which controls the level of pressure maintained by liquid boil-off.

In some advanced cryogenic setups, active refrigeration may be used to prevent boil-off, or the boil-off gas may be re-liquefied by a mechanical system.

HAZARD CLASSIFICATION

Classification of simple asphyxiants, gases under pressure, and cryogens is covered in Section 6 of the CHP. All personnel who agree to abide by this SOP are required to familiarize themselves with the contents of Section 6 of the CHP.

VOLUMETRIC EXPANSION

Cryogens expand immensely on boiling, with the gas further expanding on warming to room temperature. One liter of cryogenic liquid (or solid for dry ice) will produce the following approximate number of liters of gas on warming to room temperature at ambient pressure: Helium 700; neon 1300; nitrogen 700; argon 800; carbon dioxide 750; oxygen 800.

HAZARDS

Physical and exposure hazards associated with cryogens and their storage include:

(1) Explosion: Evaporation of cryogens in closed systems can produce pressure rises of thousands of pounds per square inch (psi), and even tens of thousands of psi if the free volume is small. Trapped cryogens are easily capable of explosively bursting all common containers and pipework. Examples of

lab incidents involving cryogens inadvertently getting in to glass flasks or cryotubes and causing them to explode on warming may be found at https://www.aiha.org/get-involved/VolunteerGroups/LabHSCommittee/Incident%20Pages/Lab-Safety-Cryogens-Incidents.aspx.

(2) Asphyxiation: The boil-off gas may displace sufficient air to cause a hazardous, or even lethal, reduced oxygen atmosphere. Low oxygen levels are exceptionally hazardous and may cause rapid unconsciousness with no prior warning. Cold dense gas may persist in confined, ill ventilated, or low-lying spaces. Chests used to store dry ice are filled with cold carbon dioxide gas — DO NOT allow your head to enter when reaching for the last blocks of dry ice.

(3) Tissue damage: Cryogens and dry ice are extremely cold. Contact with skin can lead to cold burns (frostbite), a painful condition caused by damage or death of frozen tissue.

Brief contact with droplets of liquid nitrogen usually results in no injury as a layer of gas caused by rapid boiling prevents the liquid from directly contacting skin and limits the rate of heat transfer. Liquid nitrogen held in contact with skin (e.g. by being soaked into porous gloves or getting into open-toed shoes) may cause severe injury. Surfaces cooled by cryogens may instantly freeze to skin if touched. Dry ice pressed against skin may cause rapid cold-burn. Mixing organic liquids with dry ice allows rapid heat transfer on contact with skin and can cause severe burns.

(4) Inadvertent air liquefaction: LN2-cooled surfaces (e.g., metal filling hose, a trap on a Schlenk line) may condense oxygen-enriched air. Liquefied air presents a fire or explosion hazard if it contacts combustible materials in the presence of an ignition source. Air inadvertently liquefied in vessels may cause pressure rise and physical explosion as the liquid evaporates.

GLASS DEWARS: EYE HAZARD

Dewar vessels are vacuum insulated. Thus, glass Dewars are under stress due to the external pressure of the atmosphere and may implode without warning with the ejection of shards of broken glass. Impact resistant eye protection (safety glasses or goggles) shall be worn when in the vicinity of glass Dewars. It is recommended that glass Dewars be externally protected by a plastic or metal case, or by being wrapped in tough tape (e.g. electrical insulating tape).

OPEN-NECK STORAGE DEWARS

Small (~5-20 L) open-neck metal Dewars are commonly used for storing liquid nitrogen in labs. Please refer to the Cryogens and Dry Ice Fact Sheet for guidance on safe filling of these Dewars. Open-neck Dewars must NOT be sealed in any way or they may overpressurize and burst. If a cap is used, it must be loose fitting with adequate passage for gas release.

PRESSURIZED DEWARS

Pressurized Dewars should be operated and maintained strictly in accordance with manufacturers' instructions and safety guidance. Safety checks, maintenance, and filling of pressurized Dewars should be done by authorized personnel who are appropriately trained and experienced. Manufacturer's

instructions and equipment operating manuals may be used as the basis of SOPs for pressurized Dewars. Pressurized Dewars are required to be seismically restrained (see below).

It is essential that pressurized Dewars are not overfilled, that the pressure release valve is not iced or blocked, and that emergency overpressure relief valves or bursting disks are in good condition.

Take precautions against the freezing-open of manually-operated valves. When closing cold valves, do not overtighten or thermal expansion may cause seizure after warming to room temperature.

STORAGE AND SEISMIC RESTRAINT

Cryogenic liquids shall be stored in dry areas with adequate ventilation (CHP Section 7). Storage of cryogens or dry ice in non-ventilated areas (e.g. cold rooms) is not permitted.

Large open-neck Dewars* and pressurized Dewars of any size must be seismically restrained. Liquid nitrogen freezers and cryogenic magnets should also be seismically restrained. Consult the CHP (Section 4) and EH&S Compressed Gas Cylinder Storage Fact Sheet for more information. Email labsafety@usc.edu if there are questions about specific cases.

* In general, any open-neck Dewar too large to be easily lifted and carried by hand should be seismically restrained.

LOW OXYGEN ALARMS

Low oxygen alarms may be required in cryogen storage and use areas, depending on quantity of cryogen, room size, local ventilation, and other considerations. If a low oxygen alarm is needed, it must be accompanied by appropriate signage inside and outside the room. A member of staff must be assigned to manage maintenance and testing of the alarm system in accordance with manufacturer's recommendations. Email labsafety@usc.edu for more information.

TRANSPORTATION

Personnel shall follow the directions given in the Cryogens and Dry Ice Fact Sheet. Cryogens shall NOT be transported within any enclosed space in a vehicle (e.g. passenger compartment or trunk), or in elevators with occupants.

The larger sizes of handheld Dewars are heavy. Personnel should not attempt to lift or carry Dewars beyond their comfortable physical capability. To avoid back injury, follow safe lifting practice, see Lifting and Back Safety Fact Sheet for guidance. Use a wheeled cart whenever possible.

OTHER REQUIREMENTS

All persons using cryogens or dry ice shall download and read the Cryogens and Dry Ice Fact Sheet, EH&S Compressed Gas Cylinder Storage Fact Sheet, and CHP Section 4 (seismic safety requirements), Section 6 (simple asphyxiants, GHS hazard classification), Section 7 (storage of cryogens), Section 8 (PPE and attire).

LN_2 AND GLASS VESSELS / TRAPS

Vessels cooled in liquid nitrogen may get liquid cryogen inside in one of three ways: (1) If the vessel is open to the atmosphere (intentionally, or via a crack or leak) then liquid air may condense; (2) If the vessel is connected to an argon source, or to a nitrogen source even slightly above atmospheric pressure (e.g. a Schlenk line) then liquid argon or nitrogen may condense; (3) If the vessel is closed but has a leak or crack below the level of the liquid nitrogen then liquid may directly enter.

To avoid the hazards of condensed cryogen, and potential pressure rise and explosion on warming, follow the steps below:

1. Before use, check vessels and pipework for cracks, leaks, and defects, and ensure valves have been properly closed or opened, as appropriate.

2. Vessels cooled in liquid nitrogen should be maintained under dynamic vacuum whenever possible.

3. Sealed vessels should be cooled with liquid nitrogen for the minimum possible time before doing one of the following:

(a) Apply dynamic vacuum if cooling needs to be continued, OR;

(b) Open to the air or to a nitrogen line with bubbler, then immediately withdraw the vessel from the LN2 cooling bath and allow to warm with free escape of gas.

If neither (a) nor (b) can be done, there is always a possibility liquid cryogen has entered the sealed vessel and that it may explode on warming. In such cases, use safety glasses/goggles plus faceshield and heavy gloves. Handle vessel with tongs, if possible, and allow to warm behind a blast shield.

4. At the end of use, cold traps should be backfilled with either air or nitrogen. To avoid cryogenic liquid condensation, the LN2 cooling bath should be removed as soon as possible after starting the backfilling. The trap should be allowed to warm to room temperature with provision for free escape of gas (direct vent to atmosphere if backfilled with air; bubbler of adequate capacity if backfilled with nitrogen).

5. Substitute dry ice for liquid nitrogen when possible.

Always use impact resistant eye protection when in the vicinity of vessels cooled in liquid nitrogen.

PREPARATION

- Do not handle Cryogens while working alone in the cleanroom area.
- Remove hand and wrist jewelry. Do not wear contact lens (Contact lens are not permitted in the cleanroom).

- Identify the locations of safety equipment (Eyewash and Shower station, Hazardous Waste Container, Emergency buttons and Phones).
- Save DPS emergency line 213-740-4321 into personal phone.
- Read the Safety Guideline and Material Safety Data Sheet for Cryogens.
- Wear all appropriate PPE (Safety Goggles, Face Shield for operations with splash hazard, Gloves for handling cryogens).
- Ensure an adequate supply of clean-up material is within reach in case of minor spills.
- Ensure an appropriate waste container is accessible to dispose contaminated clean-up material.
- For more hazardous work involving Cryogens restrict access to work area with sign labelled "Warning – Cryogens".
- Clearly label all containers with any liquids, including containers with water.
- Labels must include User Name, Group (PI) Name, Contact Email or Phone Number, Chemical Name, and Chemical Formula.

WASTE DISPOSAL

Cryogens may be safety disposed by allowing to evaporate in a fume hood. Slow evaporation in a well-ventilated room is permissible if the quantities are small.

If hazardous chemicals are being used, contaminated materials shall be disposed of as hazardous chemical waste. Please follow all EH&S directions (hazmat webpages, fact sheets, CHP). Please email hazmat@usc.edu if you have questions that are not answered by EH&S online resources.

CRYOGEN SPILL RESPONSE

A small cryogen liquid spill (e.g. one liter of liquid nitrogen in a large room) should simply be allowed to evaporate. If the liquid pools in one place it may freeze the floor and damage it — move the liquid around with a brush if this appears to be happening.

Spilled dry ice should be picked up with dustpan and brush, DO NOT pick up with hands.

A large cryogen spill (e.g. a burst Dewar, NMR magnet quench, or pressurized Dewar with the outlet valve frozen open) may rapidly create a harmful or fatal low oxygen atmosphere. A small spill in a confined area may do the same. IMMEDIATE evacuation of the affected area is critical. Close all doors behind you. If any personnel become unconscious DO NOT attempt rescue as you will likely become another victim. Remember, oxygen deficiency is not clearly sensed by humans and may cause loss of consciousness suddenly with no prior symptoms or warning. Call DPS and state the nature of the emergency. Hazmat will be dispatched with oxygen monitors and self-contained breathing equipment.

SKIN AND EYE EXPOSURE

Frostbitten areas should be gently rewarmed using warm water (37-40 °C; 99-104 °F); NEVER use hot water.

- The water should feel very warm but NOT hot to uninjured areas.

- A hand or elbow can be used to test the temperature if a thermometer is not available.
- Do NOT attempt to rewarm using concentrated heat sources such as heat lamps or hot air blowers.
- Do NOT rub or massage affected areas as this may cause tissue damage.

Rewarming can take up to 30 minutes if freezing is extensive. Signs of satisfactory rewarming include skin becoming a normal color or turning red due to blood flow returning, and numbness giving way to tingling/burning/painful sensations as nerve function returns.

It is recommended to always seek medical attention. Medical attention is especially important if there is persistent numbness or pain, blisters develop, the skin is broken, the cold burn is deep or extensive, or blood flow does not return after warming.

For more information, see https://www.mayoclinic.org/first-aid/first-aid-frostbite/basics/art-20056653 and https://my.clevelandclinic.org/health/diseases/15439-frostbite.

UNATTENDED EXPERIMENTS

- Chemicals may not be left unattended for more than 15 minutes.
- For unattended experiments longer than 15 minutes, notify cleanroom staff to get permission.
- The maximum time for unattended chemicals is one hour.
- Unattended chemicals require displayed signage at fume hood.
- The sign must contain the hazards of the experiment, the experimenter's name and contact information, responsible PI's name and contact information, expected date and time of disposal.
- For more information on unattended hazardous experiments, please refer to the Unattended Hazardous Operations Fact Sheet.

EMERGENCY NOTIFICATION

- Notify the Department of Public Safety (DPS) at (213) 740-4321 or (323) 442-1000. For a non-emergency, dial (213) 740-6000.
- State the nature of the emergency (e.g., injury, hazardous materials or biohazards spill, fire) and provide details.
    a) Location of injury/incident
    b) Name(s) of injured and name(s) of witness(es)
    c) Contact information (your name and call-back number)
    d) Injury/incident summary
- Notify EH&S immediately at (323) 442-2200 or injuryprevention@usc.edu to report the injury/incident.
- Notify the cleanroom staff and your supervisor.

References

- SOP – Cryogens | USC Environmental Health & Safety

- Chemical Hygiene Plan

Contributors	Revised Date
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