DREXEL UNIVERSITY
Department of
Environmental
Health & Safety

SOP Number: 0081

Standard Operating Procedures for Handling, Storage, and Disposal of Cryogenic Liquids

Purpose:

The purpose of this document is to develop safe working, handling and emergency procedures for the laboratory personnel when working with cryogenic liquids.

Overview:

Cryogenic liquids, or Cryogens, are liquefied gases that are kept in their liquefied state at very low temperatures. Typically, cryogenic liquids have boiling points below -51ºC (-60ºF or 222K). All cryogenic liquids are extremely cold and small amounts of liquid may expand into very large volumes of gases when heated or even when exposed to room temperatures.

Cryogenic liquids are generally divided into three categories:

- Inert Gases: Cryogenic liquids consisting of inert gases generally do not burn or support combustion and have little or no toxic effects. However, they can be extreme cold hazards and they may displace oxygen as they evaporate leading to asphyxiation. Examples include nitrogen, helium, neon, argon, and krypton.
- Flammable Gases: These are cryogenic liquids that produce a gas that can burn in air. Common examples include hydrogen, methane, and liquefied natural gases.
- Oxygen: In addition to being an extreme cold hazard, liquid oxygen is a very concentrated oxygen source. Many normally non-combustible materials may burn in the presence of liquid oxygen. Organic materials may even explosively react on contact with liquid oxygen.

Hazards

The use of cryogenic liquids has several potential hazards. Always review the Safety Data Sheet (SDS) and this SOP prior to their use. Examples of hazards may include:

- Adhesion: Cold surfaces of equipment and piping containing cryogenic liquids can cause skin to stick to the surface. Trying to remove yourself from the surface may tear your skin.
- Asphyxiation Hazard: The gases and vapors of a cryogenic liquid tend to be very cold and heavier than air. The gasses do not disperse well and stays close to the floor. The gases can displace air especially in enclosed or confined spaces with poor ventilation. Small amounts of liquids can evaporate into large volumes of gas. For example, at room temperature 1 liter of liquid nitrogen forms 695 liters of nitrogen gas. Coma or death may occur due to oxygen deficiency in enclosed or poorly ventilated spaces. NEVER

enter an oxygen deficient area even to rescue someone. Oxygen level sensors may be required in some storage or work areas.

- Cold Embrittlement: Some materials such as rubber, plastic, common glass, and carbon steel, become brittle and even shatter at low temperatures. Avoid using these materials with cryogenic liquids.
- Extreme Cold Hazard: Contact of liquid or vapor may cause frostbite or damage similar to thermal burns (*often called cold burns*) to skin, eyes, and lungs with even brief contact. Often there is little or no pain on contact, but this can greatly intensify as the frozen area thaws.
- Flammability Hazard: The use of Cryogenic liquids has several situations may produce flammability hazards:
    - Explosion due to Rapid Expansion: Without adequate venting or properly functioning pressure-relief devices on the containers, enormous pressures can build up, potentially resulting in an explosion. External fires or damage to the container's insulation may also result in an explosion due to a rise in temperature. These containers should have a back-up device such as a frangible (*bursting*) disc. Even in normal circumstances, the containers may be at high pressure, so appropriate precautions must be taken. Never store cryogenic liquids near a heat source (*for example, open flame or a radiator*).
    - Fire Hazards: Flammable gases such as hydrogen, methane, liquefied natural gas, and carbon monoxide can burn or explode. Hydrogen is particularly dangerous as it forms flammable mixtures with air in concentrations ranging from 4% to 75%. It is also easily ignited. Never store flammable gases or liquids near an ignition or heat source.
    - Liquid Oxygen Hazards:
        - Liquid Oxygen has 4000x more oxygen by volume than air. The high concentration of oxygen may result in normally non-combustible materials, such as carbon steel, stainless steel, aluminum, zinc, and Teflon, to ignite in the presence of liquid oxygen.
        - Organic materials may react explosively on contact, especially if a flammable mixture is produced.
        - Clothing splashed with liquid oxygen can remain highly flammable for hours afterwards.
        - Stored Oxygen must be separated from flammables and combustibles by 20 feet or a half-hour fire wall.
        - Ignition sources are not permitted near liquid oxygen.
        - Keep liquid oxygen and its container clear of grease, oil, asphalt, kerosene, cloth, tar, and dirt that may contain oil or grease. These may

react violently with oxygen if ignited by a spark or even a mechanical shock.

  - Oxygen-Enriched Air: Some cryogenic liquids, such as nitrogen and helium, are so cold, that they may liquefy the air on contact. The nitrogen from the frozen air tends to evaporate first, leaving a liquid air with a high concentration of oxygen, having similar properties as the liquid oxygen mentioned above. This cryonic oxygen-rich liquid often forms on the outside of transfer lines.

- Liquid Helium Hazards: Special precautions should be taken with liquid helium as 4^{o}Kelvin is sufficient to cause most other gases to freeze solid. Liquid helium systems must prevent back flow of air or other gases as they may freeze within the container or delivery lines. This resulting ice plug can potentially clog up the vents and lines resulting in a container building in pressure to potentially explosive levels.
- Obscured Vision: The vapor formed from cryogenic liquids tends to fall down forming a ground-level fog that obscured the floor. Beware of trip hazards.
- Toxic Hazards: Some cryogenic liquids are toxic (ex. liquid carbon monoxide) which can release large quantities of deadly carbon monoxide gas. Always review the Safety Data Sheet (SDS) before using a cryogenic gas.

Standard Operating Procedures:

Handling

1. Be familiar with hazards associated with cryogen use. Review the Safety Data Sheet and this SOP before its use.
2. Work in an open and well-ventilated location. EHS may require oxygen level detection in certain situations.
3. Always wear safety goggles/safety glasses and face shield.
4. Do not leave skin exposed. Do not wear metal jewelry or watches as metal can become frozen to the skin (arm, wrist, fingers, etc.).
5. Examine containers and pressure relief valves for signs of defect, damage, neglect, or unauthorized modifications. Never use a container that has defects. Ask the cryogenic vendor for assistance with questions on cryogenic equipment and pressure relief valves.
6. Ensure that all equipment and containers are free of oil, grease, dirt, or other materials which may lead to flammability hazard upon contact with liquid oxygen. Dirt may also cause valves to seize up.
7. Select working materials carefully. Cold cryogenic liquids may alter the physical characteristics of many materials making them brittle and fail.
8. Verify there is pressure relief for any place that there can be a pressure build-up.

9. It is the responsibility of the Principal Investigator to ensure lab personnel are properly trained in the safe use of cryogenic materials.
10. Always wear appropriate personal protection equipment including loose fitting insulated gloves made for cryogenic work, face shield used in combination with splash goggles or safety glasses, and appropriate apron, lab coat, or overalls. There should be no pockets exposed that liquid can get trapped inside. Rubber or latex gloves will only become brittle on contact and cotton gloves may wick up the cold liquid. Appropriate laboratory attire must be worn while handling cryogenic liquids (no open-toed shoes, no mesh shoes, no shorts, no exposed skin, etc).
11. Never allow any unprotected part of the body to touch non-insulated pipes or vessels which contain cryogenic liquids. Tissue damage may result.
12. Use a suitable hand truck for all container movement.
13. Do not drop, tip, or roll containers on their sides. All cryogenic systems and Dewars must have pressure relief valves to release excessive pressure. Dewar flasks should have loose fitting lids. The pressure relief valves should be inspected regularly.
14. Do not lower warm experiments into Dewars of cryogen.
15. Provide proper venting for the Dewars used in experiments.
16. Dewars used in experiments involving strong magnetic fields must be non-magnetic.
17. Never force (i.e. use a wrench or lubricant) or modify any knob or valve on the container.
18. Do not remove or interchange connections. Use only the proper connection. Do not use adapters.
19. Discontinue use and contact your supplier if you experience any difficulty in operating a container valve or with the container connections.
20. Use only fitted transfer tubes designed for use with the Dewar container. Damaged transfer tubes should be replaced. Do not handle transfer tubes with your bare hands as the fitting is not insulated.
21. Select working materials carefully as cryogenic temperatures may alter the physical characteristics of many materials (i.e. make them brittle).
22. When transferring to a secondary container, ensure the vessel is dry and do not fill the secondary container to more than 80% of capacity (60% if the room temperature is likely to be above 30^{o}C). Pour into the vessel slowly to minimize splashing, spilling, and thermal shock to the vessel. Avoid shallow and wide-necked vessels to prevent excess evaporation and the possibility of oxygen enrichment. Never use a funnel.
23. Immediately re-cap any container to prevent atmospheric moisture from entering and forming an ice plug in the opening.
24. Use care in transporting cryogens; do not use fragile containers. Use a hand truck or the lowest shelf of a cart for transport of cryogens.

25. When available, use service elevators for transferring unsealed containers of cryogens. Avoid passenger elevators when possible. Keep passengers off the elevator while a cryogenic liquid or gas is transported.
26. Use tongs or similar devices when placing objects into or removing them from cryogenic liquids.

Storage

1. Store cryogens in well-ventilated areas to prevent oxygen deficiency. EHS may require oxygen level detection in certain situations.
2. Use only approved storage vessels that have pressure relief valves.
3. Never adjust, block, or plug a pressure relief valve. The vendor is required to check the pressure relief valve before filling the Dewar.
4. Avoid contact of moisture with storage containers to prevent ice plugs in relief devices.
5. Periodically check container necks for ice plugs; core out ice plugs if present.
6. Keep all heat sources away from cryogenic liquids.
7. Do not store or use cryogens in walk-in cold rooms, refrigerators, sealed rooms, or basements. They may not have sufficient air exchange and could become hazardously oxygen deficient.
8. Cryogenic containers, whether empty or full, must be stored within the lab or an approved storage area where they are accessible to relevant personnel only. They are not to be left in the hallways where passersby may risk exposure. It is a violation of the fire code to store them in egress hallways.
9. Stored Liquid Oxygen must be separated from flammables and combustibles by 20 feet or a half-hour fire wall.
10. Ignition sources are not permitted near liquid oxygen or flammable cryogenic liquids.
11. Keep liquid oxygen and its container clear of grease, oil, asphalt, kerosene, cloth, tar, and dirt that may contain oil or grease. These may react violently with oxygen if ignited by a spark or even a mechanical shock.

Disposal

1. Small amounts of cryogenic liquids may be evaporated in chemical fume hoods or another well-ventilated area.
2. NEVER pour cryogenic liquids down the sink – The liquid will crack the pipes causing potentially dangerous leaks.
3. Venders and Suppliers will often remove unwanted cryogenic liquids. Contact EHS at safeheal@drexel.edu if you need assistance.

Spill Procedures

1. Evacuate the room and allow the liquid to evaporate for small spills of inert cryogenic liquids less than 500ml. Contact the 24 -Hour Call Center at (215) 895-2222.
2. For 1) large spills, greater than 500 ml, 2) if the valve is stuck open, or 3) any amount of flammable, toxic, or oxidizing cryogenic liquids, shut off all ignition sources if it can be safely done, evacuate all personnel, and contact 24 -Hour Call Center at (215) 895-2222 or 911.
3. Inform EHS of any spill at (215) 895-5919.
4. Never rub exposed flesh or expose it to dry heat. A warm water bath (not above 40°C) should be used only if directed by an emergency responder.
5. Inspect the lab for damage after it returns to room temperature and has been properly vented. Notify the PI and/or Facilities if there is any damage to the lab or any equipment.

Common Cryogenic Liquids:

Cryogen	Boiling Point (1 atm) °C (°F)	Critical Pressure, psig	Liquid Density, g/L	Gas Density (27°C), g/L	Liquid-to-Gas Expansion Ratio	Type of Gas
Argon (Ar)	-186 (-303)	710	1402	1.63	847	Inert
Carbon Dioxide (CO_2)	-79 (-110)	1056	1010	1.98	450	Inert
Helium (He)	-269 (-452)	34	125	0.16	757	Inert
Hydrogen (H_2)	-253 (-423)	188	71	0.082	851	Flammable
Nitrogen (N_2)	-196 (-321)	492	808	2.25	696	Inert
Oxygen (O_2)	-183 (-297)	736	1410	1.4	860	Oxygen
Methane (CH_4)	-161 (-256)	673	425	0.72	650	Flammable

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Standard Operating Procedure Training Documentation

Please fill out the form completely. Print a copy and keep with the hard copy of the SOP.

Standard Operating Procedure:_____
(*Chemical and/or Procedure*)

Principal Investigator:_____

Department:_____

Location(s) covered by this SOP:_____
(Building and Room Number)

Documentation of Training *(signature of all users is required)*

- ✓ Prior to conducting any work with _____, designated personnel must provide training to his/her laboratory personnel specific to the hazards involved in working with this substance, work area decontamination, and emergency procedures.
- ✓ The Principal Investigator must provide his/her laboratory personnel with a copy of this SOP and a copy of the SDS provided by the manufacturer.
- ✓ The Principal Investigator must ensure that his/her laboratory personnel have completed the appropriate laboratory safety training or refresher training within the last year.

I have read and understand the content of this SOP:

Name	**Signature**	**Date**
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____