

4.04 CRYOGENIC LIQUIDS SAFETY PROGRAM

Cryogenic liquids are very cold substances [gases which have been condensed into liquids at extremely low temperatures], and are used in research to provide extremely low temperatures for frozen storage and experimentation. Hazards associated with their use include personnel exposure (cold burns, frostbite), material and construction incompatibility, high pressure gases, explosions, implosions, toxicity, and asphyxiation. This document describes administrative controls necessary to protect personnel from contact or exposure during handling of cryogenic liquids and materials.

A. SCOPE

This program provides guidelines for the safe use of cryogenics, and applies to all personnel and laboratories at the University, including but not limited to research, clinical, instructional, analytical, and/or academic entities.

B. DEFINITIONS

Cryogenic Liquid (Cryogen) – Gas that has been transformed into an extremely cold refrigerated liquid and stored at temperatures below minus 130 degrees Fahrenheit or minus 90 degrees Celsius. Examples of gases commonly handled as cryogenic liquids include oxygen, nitrogen, argon, neon, krypton, xenon, hydrogen and helium.

Liquefied Compressed Gases – Elements or compounds that have boiling points from around -130°F up to 30°F at atmospheric pressure. Examples include carbon dioxide, nitrous oxide, anhydrous ammonia, chlorine, several fluorocarbons, butane, isobutene and propane.

Dewar – Open-mouthed, unpressurized, vacuum-jacketed vessels used to hold cryogenic liquids (usually argon, helium, nitrogen, or oxygen). Five to 200-liter Dewars are available. Product may be removed from small Dewars by pouring, while larger sizes will require a transfer tube.

Cryogenic Liquid Cylinders – Insulated, vacuum-jacketed pressure vessels equipped with safety relief valves and rupture discs to protect the cylinders from pressure buildup. These vessels operate at pressures up to 350 psig and have capacities between 80 and 450 liters of liquid. Product may be withdrawn as a gas by passing liquid through an internal vaporizer or as a liquid under its own vapor pressure.

Laboratory - A workplace where relatively small quantities of hazardous chemicals are used on a non-production basis and chemical manipulations are carried out on a “laboratory scale.”

Laboratory Scale - Work with substances in which the containers used for reactions, transfers and other handling of substances are designed to be easily and safely manipulated by one person.

Material Safety Data Sheet (MSDS) – An informational tool developed by chemical manufacturers containing the following information for a hazardous chemical: substance identification and synonyms, hazardous components (if mixture), physical data, fire and

explosion data, toxicity data, health effects and first aid, reactivity, storage and disposal procedures, spill and leak procedures, and recommended protective equipment. An MSDS can be obtained from the chemical suppliers and internet sites and should be available to those working with the material.

Personal Protective Equipment (PPE) - Barrier protection which shall be worn by workers to guard against skin or eye contact with cryogenic liquids, examples of which may include safety glasses with side shields, goggles, face shields, thermal-insulated gloves, aprons, closed shoes, and/or even pot holders. Splashes are common, and safety glasses, at a minimum, must be worn at all times when working with cryogenic materials.

Physical hazards - Cryogenic liquids can cause very severe cold burns upon eye or skin contact, the tissue damage that results is similar to that caused by frostbite or thermal burns. It is not unusual for spills and splashes to become trapped under rings, bracelets, watchbands, or inside gloves, and this can result in serious and painful frostbite. Particular care must be taken to prevent uninsulated vessels containing cryogenic liquids from coming into contact with unprotected parts of the body, since these extremely cold materials can become firmly bonded to the skin such that separation is not possible without serious injury (torn flesh).

Special Hazards of Liquid Cryogenics –

- The properties of some materials change drastically at very cold temperatures: ductile materials can become brittle, material shrinkage can exceed anticipated values, and leaks can develop that are undetectable even under pressure. Because cracks may develop at cryogenic temperatures, and if these cracks close on warming, the vaporizing fluid could expand and shatter the vessel (necessitating the use of pressure relief devices).
- Liquid cryogenics warmed above critical temperatures will generate high pressure, causing a confining vessel to rupture or even explode. For example, small containers, such as stoppered test tubes, have over-pressured and produced flying fragments. Fully pressurizing a gas into a cryogenic liquid at room temperature is usually not feasible, e.g., the pressure required to maintain liquid nitrogen at room temperature is 43,000 psi.
- Cryogenics can create oxygen deficiency because they have large liquid-to-gas expansion ratios (generally >700). A small liquid spill produces a large volume of gas that can displace the air in a confined space, thus creating a serious oxygen deficiency that can suffocate occupants of the area.
- Some liquid cryogenics are chemically very reactive (e.g., oxygen), others are flammable (e.g., hydrogen and methane), which can lead to fires.
- Cryogenic fluids with a boiling point below that of liquid oxygen may condense oxygen from the air if exposed to the atmosphere. Because oxygen does not evaporate as rapidly as liquid nitrogen, it may accumulate and may cause violent reactions with incompatible materials in the system. Oil and grease will spontaneously ignite/explode if exposed to liquid oxygen.

Chemical Hygiene Plan - A written program developed and implemented by the laboratory management which sets forth procedures, equipment, personal protective equipment (PPE) and

work practices that are capable of protecting employees from adverse health hazards associated with the use of hazardous chemicals and materials. In essence, it is a general lab safety manual.

Standard Operating Procedure (SOP) - A concise document that gives safety instructions specific to experimental materials and methods in a specific laboratory, setting or operation.

C. RESPONSIBILITIES

1. Safety and Risk Services (SRS) is responsible for:

- Developing and implementing a University-wide program;
- Providing technical assistance and monitoring compliance with this program;
- Providing general training to Principal Investigators and other primary users;
- Conducting exposure assessments and evaluating exposure control measures;
- Investigating laboratory accidents and performing risk assessments;
- Maintaining employee exposure, training and safety audit records;
- Developing a laboratory self-audit form; and
- Conducting periodic audits of laboratories to ensure that adequate facilities, ventilation, PPE, and other equipment are provided for the safe use of cryogenes.

2. Deans, Directors and Department Heads responsibilities include:

- Support and work toward departmental compliance with all the procedures outlined in this program, so as to minimize risk; and,
- Implement reasonable precautions to meet the intent/purpose of these guidelines.

3. The Principal Investigator/Director/Supervisor of the laboratory is responsible for:

- Developing and training employee/students in Standard Operating Procedures (SOP's) that address the specific safety procedures to be used in the laboratory;
- Training employees/students in hazard awareness, PPE use, and chemical safety;
- Arranging for immediate emergency response, if necessary, for spills, injuries, etc;
- Implementation of recommended remedial actions;
- Establish guidelines for employees/students working alone during off hours, regarding what procedures can and cannot be performed during off hours to assure their safety;
- Conducting periodic audits to ensure that all employees/students are complying with SOP's and are implementing this and other safety programs in the laboratory;
- Providing proper area-specific PPE (goggles, insulated gloves, face shields, safety glasses, aprons, etc.), and enforcing the appropriate use of the PPE; and,
- Documenting all training, audits, SOP's, medical surveillance, PPE use, injuries, etc.

4. The Chemical Safety Officer's (the Principal Investigator/Director/Supervisor may also be the CSO of the laboratory) responsibilities are:

- Working with administrators and other employees to develop and implement the Standard Operating Procedure for Cryogenics;
- Training all newly-hired laboratory employees about the specific physical hazards associated with the cryogenics present in the laboratory, and the required PPE;
- Updating the chemical inventory list and MSDS's as necessary;
- Ensuring the laboratory self-audits are conducted, and that the required PPE is being used;
- Acting as a liaison between the laboratory and SRS; and
- Providing area-specific chemical safety training.

5. Laboratory personnel are required to:

- Know the provisions of the laboratory's Standard Operating Procedure for Cryogenics;
- Review chemical hazard information detailed on MSDS before beginning work with cryogenics.
- Conduct assigned tasks in a safe manner, while using the required PPE properly;
- Comply with this safety program and any further safety recommendations initiated by the Principal Investigator;
- Report accidents, any potential job-related injuries or illnesses, health and safety concerns, or unsafe conditions to their supervisor; and
- Use Personal Protective Equipment and engineering controls as instructed.

D. STANDARD OPERATING PROCEDURES

Read the MSDS and safety precautions for all cryogenics used, and incorporate these precautions into specific written Standard Operating Procedures in collaboration with Safety and Risk Services. These SOP's should include many, if not all, of the following guidelines:

1. Use of Cryogenic Liquids

Cryogenic liquids have properties that make them more dangerous to use than other liquids: extremely cold temperatures, high liquid-to-vapor expansion ratios, and flammability for certain liquids. Skin or eye contact with cryogenic liquids, cold equipment and materials that are used in conjunction with cryogenics, or splashing liquid can cause severe tissue damage such as cold burns, frostbite, ripping/tearing of the flesh, and eye damage. Vapors from boiling liquids can also cause eye damage, frostbite to the skin, and oxygen deficient environments. To minimize exposure during use, implement the following procedures that may be applicable:

- Perform a Personal Protective Equipment (PPE) assessment to determine the level of protection needed for the task. Typical PPE used to work with cryogenic liquids includes safety goggles, insulated gloves, lab coat or apron, and a face shield. Gloves should be loose enough to easily toss off in the event of liquid cryogen entering the gloves.
- **At a minimum, safety glasses with side shields are required whenever cryogenic liquids, exposed to the atmosphere, are present** (goggles provide the best protection for the eyes).

- Long sleeve shirt and pants, and a buttoned lab coat should be worn. Cuffless pants should be worn over the shoes. Shoes must be closed-toed leather or safety shoes. As with any lab, never wear sandals. Avoid jewelry (rings, watches, ear rings, nose rings, etc.) or other materials that could trap spilled liquid to the skin or other body part.
- Stay out of the vapor pathway, but if unavoidable, hold breath until out of the cloud.
- Do not use fume hoods when working with flammable cryogenics, unless the hood and appurtenances are explosion proof.
- Avoid touching liquid cryogen, even with gloves.
- Keep metal and glass dewars uncovered or cover with a loose-fitting cap. Shield or tape the external surfaces of a glass Dewar to prevent shattering in case of breakage.
- Cryotubes containing samples stored under liquid nitrogen may explode without warning. Tube explosions are caused by liquid nitrogen entering the tube through minute cracks and then expanding rapidly as the tube thaws. Cryogenic storage vials are designed for vapor phase storage in the extremely cold nitrogen gas that sits just above the reservoir of liquid nitrogen in the bottom of the freezer or Dewar. If the freezer/dewar is overfilled with liquid nitrogen and the vials are immersed, leakage of liquid nitrogen into the vial occurs. To avoid this problem, do not overfill the freezer/dewar with liquid nitrogen. As a precaution, slowly remove vials from the Dewar, holding the vials in the neck of the Dewar for a moment before bringing them into room atmosphere. It is best if cryotubes are kept in a heavy, walled container or behind a safety shield while warming (a tube that is going to explode will usually do so early in the warm-up process). Cryotubes should never be re-used.
- Periodically inspect equipment and remove ice and frost blockages from openings to prevent over pressurization (LN₂ vents will always build frost and ice on filling).
- Do not tamper with pressure relief valves. Report any leaks or improperly set relief valves to the vendor/CRLS filling tanks. Constant (non-stop) venting is a sign of a broken tank.
- Equipment should be kept clean without the use of corrosive cleaning materials that could damage the metal jacket. Beware of rust or dents in Dewars.
- SRS may recommend the installation of oxygen detection systems and alarms for cryogenic liquid storage or use areas depending on location, ventilation rates, and quantity of material stored.
- Use only vessels designed for extreme cold. Not all Dewars are rated for liquid nitrogen. Always follow manufacturers' guideline for use of cryogen vessels of any size.
- Do not interchange adapters between different cryogenics that are not compatible. Do not alter, obstruct, defeat, or tamper with relief valves, rupture discs, or fittings.
- Handle objects in direct contact with cryogenic liquids with tongs, potholders, and/or insulated gloves. Do not touch bare metal or other conductive surfaces without appropriate personal protective equipment.
- Ensure containers are properly labeled. Do not destroy or remove identification tags or labels.
- Insulate pipes and other conductive surfaces, and otherwise design a cryogenic system with appropriate materials and provide enough headspace in containers or piping for liquefied gases to expand.

- Do not interchange adapters between different cryogenics that are not compatible. Do not alter, obstruct, defeat, or tamper with relief valves, rupture discs, or fittings.
- Always use care when handling equipment. Damage to containers or cylinders could result in the loss of vacuum and cause increased evaporation.

2. Dispensing and Transport of Cryogenic Liquids

Special precautions must be taken to prevent a spill while dispensing or transporting cryogenics 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 exposure:

- Always wear proper PPE when dispensing or transferring cryogenic liquids. **At a minimum**, safety glasses with side shields are required whenever cryogenic liquids are poured, for open transfers, and if the fluid in an open container is likely to bubble.
- When obtaining cryogenic liquid from a large dispensing Dewar or cylinder, cool the secondary container by adding a little cryogenic liquid first, dispense slowly to mitigate thermal stress, stay in constant attendance of the filling operation, and do not overfill.
- When manually pouring cryogenic liquid into a smaller Dewar, assure that the secondary container is secured, use a tipping stand if feasible, pour slowly to prevent excess splashing, thermal shock or excessive pressure buildup, and do not overfill.
- **AVOID TRAVELING IN AN ELEVATOR WITH A DEWAR.** Exceptional care must be exercised when transporting liquid cryogenic containers (>10 liters) in elevators. Elevator failures may be dangerous because the oxygen in this restricted space will be displaced, if the container failed or leaked. If possible, transport the container only on a reliable freight elevator that is not generally used for personnel transport. If a freight elevator is not available, a passenger elevator can be used. After the cryogenic liquid container is placed in the elevator and a danger sign posted, the elevator should be locked out to all other users. The sender should remain outside the elevator and activate it. If feasible, another person could be available on the receiving floor to take the cryogenic liquid container off the elevator at its destination. If it is absolutely necessary to have an attendant in the elevator with the container, an escape-pack supplemental-breathing apparatus must be carried in the elevator, and be readily available to the trained attendant.
- Transfer cryogenics slowly to prevent thermal shock or excessive pressure buildup. Exercise great care when using a funnel; do not fill above the funnel neck!
- Persons filling any containers or cylinders must be in constant attendance during the filling operation.
- For short distances inside buildings, it is acceptable to hand-carry a smaller dewar of liquid nitrogen *which has no handles*, if the Dewar (no Styrofoam cups) is your only load, the vessel has a venting lid, you are using both hands, and wearing PPE (glasses, gloves).
- The best transport for larger (>10 liters) cryogenic liquid containers is by Dewars (>10 liters) equipped with carrying handles.

- Push wheeled containers and move other containers with a suitable hand truck. Do not place any container on its side during transportation of any liquid cryogenic material.

3. Storage of Cryogenic Liquids

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

- 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 have the external surfaces thoroughly taped, or should be replaced.
- Do not store cryogenic liquids with corrosive or flammable chemicals.
- Storage units of cryogenic liquids should be placed so that vents and openings are oriented away from personnel and lab equipment.
- Storage of cryogenic liquid Dewars in hallways (security issue!), and in unventilated closets, environmental rooms, cold rooms and stairwells is prohibited.
- Dewars filled with cryogenic liquids must be stored in areas designed for such storage. Contact SRS at 277-2753 to evaluate potential storage locations.
- SRS may recommend the installation of oxygen detection systems and alarms for cryogenic liquid storage or use areas depending on location, ventilation rates, and quantity of material stored.
- A minimum of six measured air changes per hour is recommended for rooms in which less than 10 liters are stored, ten air changes per hour for storage of 10-180 liters and fifteen air changes per hour for storage of amounts in excess of 180 liters.

4. Special Precautions for Flammable Liquids and Oxygen

Flammable cryogenic liquids like methane and hydrogen introduce an additional hazard. Oxygen does not burn, but accelerates and supports combustion. High concentration oxygen atmospheres substantially increase combustion rates of other materials and may form explosive mixtures with other combustibles. It is important to implement the following procedures when using flammable cryogenics and oxygen.

- Contact SRS at 277-2753, to assist in the assessment of administrative and work practice controls, if you plan to work with these materials.
- There are several industry guidelines that refer to flammable liquids that should be considered in addition to these recommendations (e.g. Air Products Safetygrams, etc.).
- All combustible materials should be kept away from flammable cryogenic liquids and oxygen. No sources of ignition should be present in this area.
- Oxygen Dewars and equipment should be kept very clean. Surface contamination, especially organic materials could become ignited if oxygen leaks from the Dewar and provides a local oxygen enriched area.

- Stationary equipment should be properly grounded and mobile equipment should be properly bonded when dispensing (See Related Documents for more detailed standards for electrical requirements).
- Valve operation should occur very slowly to prevent ignition of contaminants in the system. Hydrogen venting should be independent from other ventilation systems and may require a nitrogen purge capability.

5. Special Precautions for the Use of Cold Traps in Liquid Nitrogen

Cold traps are used for protection of many types of instrumentation, building vacuum systems (closed or open), water aspirators, and/or vacuum pumps. Cold traps prevent the introduction of liquids and vapors into and out of the system by providing a low temperature surface for molecules to condense. Because extreme care must be employed when using liquid nitrogen (LN₂) in cold traps, the following procedures must be implemented to prevent over pressurization and explosion:

- In the event that the system is opened with the trap still in place, there is a possibility that oxygen will condense out of the air and combine with the organic material inside the trap. **DO NOT RECLOSE THE SYSTEM**, as this might result in an over pressurization and possible explosion.
- Liquid nitrogen can condense oxygen from the air. This is most alarmingly demonstrated if a person leaves his/her vacuum pump's cold finger in a Dewar of liquid nitrogen overnight. In the morning the cold finger will contain **LIQUID OXYGEN** up to the level of the nitrogen remaining in the Dewar.
- If you suspect liquid oxygen has condensed in a cold trap, then shield the trap (with an explosion shield, closed hood sash, etc.), post a sign indicating the danger, and allow the trap (vented to the atmosphere) to slowly warm to room temperature.

6. Emergency Procedures

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. Virtually all cryogenic gases are odorless, colorless, tasteless, and inert. Simply reducing the oxygen content in a room below 19.5 % is considered (by OSHA) sufficient to cause an oxygen deficient environment. Implement the following procedures to minimize the risk of asphyxiation:

- Periodic equipment inspections, removal of frost and ice blockages, and replacement of damaged or old storage units will reduce the probability of the catastrophic failure of a storage unit.
- If ventilation in the room is less than six measured air changes per hour, contact PPD to increase the air flow through the ventilation system. If this is not feasible, then contact SRS about installing an oxygen level detection alarm.
- If a spill occurs, immediately exit the area. With adequate ventilation, it may be appropriate to return to the area after thirty minutes. For large spills, contact SRS

immediately to monitor oxygen levels in the area and determine when it is safe to re-enter.

- If experiencing symptoms such as lightheadedness, dizziness, or confusion, immediately seek fresh air and receive/seek medical attention.
- If an employee becomes unconscious in a cryogenic liquid storage area that is a confined space, they should be retrieved by personnel using proper PPE (such as a Self Contained Breathing Apparatus). Campus Police should be immediately notified at 277-2241 to coordinate emergency rescue services.
- Once such unconscious personnel have been removed to fresh air, 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.
- Immediately remove any clothing that has been contaminated. In the event of clothing contamination with oxygen, hydrogen, or carbon monoxide, it may be important to remove clothing, evacuate personnel from the room/facility, and keep away from ignition sources.
- Flush or soak the area with lukewarm water.
- Do not apply dry heat or rub damaged flesh or eyes.
- Employees should notify their supervisor of injuries and report to EOHS for medical evaluation and follow-up.

Note: Extracted in part from the Occupational Safety and Environmental Health Guideline of the University of Michigan.

Relevant Physical Properties of Cryogenic Liquids

Cryogenic Liquid	Carbon Dioxide CO ₂	Xenon Xe	Methane CH ₄	Oxygen O ₂	Argon Ar	Carbon Monoxide CO	Nitrogen N ₂	Neon Ne	Hydrogen H ₂	Helium He
Boiling Point, 1atm ⁰ F (°C)	-108 (-78)	-163 (-108)	-259 (-161)	-297 (-183)	-303 (-186)	-313 (-192)	-320 (-196)	-411 (-246)	-423 (-253)	-452 (-268)
Volume Expansion Ratio ¹	790	559	625	860	842	680	696	1445	850	745
Liquid Density ² , g/l	1560	3060	417	1137	1394	785	801	1201	71	125
Gas Density STP, g/l	1.96	5.85	0.71	1.43	1.78	1.25	1.25	0.90	0.09	0.18
Flammable	No	No	Yes	No ³	No	Yes	No	No	Yes	No

- 1) From liquid at 1 atmosphere and boiling point, to gas at 70⁰F and 1 atmosphere (Handbook of Compressed Gases, 3rd Edition).
- 2) Density at boiling point and 1 atmosphere (Handbook of Compressed Gases, 3rd Edition).
- 3) Although oxygen does not burn, by itself, it will support and significantly accelerate combustion. Oxygen-enriched atmospheres may lead to violent reactions with incompatible materials, such as rapid combustion or explosions.