SAFETY MANUAL

FOR CRYOGENIC LIQUIDS AND CRYOGENIC DEVICES

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CONTENT

INTRODUCTION

This manual contains important information about cryogenic liquids and the Liquid Nitrogen (LN_2) Production System that you have bought. Please read this manual before using your plant.

1. NITROGEN

LN_2 is inert, colorless, odorless, non-corrosive, non-flammable, tasteless, extremely cold, and has no warning properties. Special care must be taken by personnel who handle or work in areas where LN_2 is used. Nitrogen is not toxic, but it acts as a asphyxiant at high concentrations.

Nitrogen has a boiling point of -196°C. The area which its used should be well ventilated since it is an asphyxiant gas. Otherwise the oxygen in the air decreases and asphyxia hazard arises.

While LN_2 boiling, its volume increases. One liter of LN_2 expands around 694 liter when it vaporises at room temperature, so while transporting LN_2, it is important to have sufficient ventilation in the area.

LN_2 carrying sealed containers may be exploded due to pressure resulted from the expansion of the gas. For this reason, liquid nitrogen storage containers and safety equipment should be controled carefully and their maintenance should be done with care.

Table 1: Physical and Chemical Properties of Liquid Nitrogen

Chemical Formula	N_2
Molecular Weight (g)	28.01
Boiling Point (1atm)	-195.8°C
Freezing point (1atm)	-210°C
Density, liquid @1atm on Boiling point	808.5 Kg/m^3
Density, gas,@1atm,Room Temperature	1.16 Kg/m^3
Liquid to vapor expansion ratio	1 to 694

1.1. DANGERS AND HEALTH PROBLEMS THAT CRYOGENIC LIQUIDS MAY CAUSE

Asphyxiation: Cryogenic liquids have high expansion and evaporation rate. The volume of evaporated gas is hundreds of times larger than the volume of the liquid phase and this results in replacement of nitrogen with the oxygen in the air. If the oxygen content in the air drops below 19%, asphyxiation risk arises. For this reason, liquid nitrogen or other cryogens should not be stored or used in poor ventilated areas.

Typical symptoms of oxygen depletion arising from evaporation of liquid nitrogen is given below.

Table 2: Typical Symptoms due to Oxygen Depletion

19%-15%	Reduction of physical and intellectual performance without the sufferer being aware.
15%-12%	Deep breaths, fast pulse, coordination difficulties
12%-10%	Vertigo, false judgement, lips slightly blue
10%-8%	Nausea, vomiting, unconsciousness
8%-4%	Death within 8 minutes, brain damages within 4-8 minutes
4%	Coma within 40 seconds, no breathing, death

There are 3 main sources of gaseous Nitrogen [1].

- Natural evaporation from dewar.
- Evaporation during dewar filling and top-up
- Spillage of LN_2.

Table 3: Oxygen concentration, %: effect of evaporation; 0.4 air changes/hour

Room volume m³	**Volume of Liquid Nitrogen,liter**										
	10	25	50	75	100	150	200	250	300	400	500
15	21.0	21.0	20.9	20.9	20.8	20.8	20.7	20.6	20.5	20.4	20.2
25	21.0	21.0	21.0	20.9	20.9	20.9	20.8	20.8	20.7	20.6	20.5
50	21.0	21.0	21.0	21.0	21.0	20.9	20.9	20.9	20.9	20.8	20.8
75	21.0	21.0	21.0	21.0	21.0	20.9	20.9	20.9	20.9	20.9	20.9
100	21.0	21.0	21.0	21.0	21.0	21.0	21.0	20.9	20.9	20.9	20.9

a. **Natural Evaporation:** Of particular concern are mornings because several hours will have elapsed since the room was entered, doors opened, etc. Table 3 gives an approximate idea of the degree of danger. The important parameters are:

- Volume of the room
- Volume of LN_2 in store
- The number of air changes per hour
- The rate of LN_2 evaporation, which depends on the integrity of the insulation

b. **Topping-Up / Filling:** Top-up / filling loses around 10% of the topping up volume so: 25l top-up loses 2.5l LN_2, producing 1735 litres of gas. So filling dewars has much more effect on oxygen depletion than does normal storage. Table 4 shows the likely effects for a range of LN volumes and room sizes. The calculations assume an air change rate of 0.4 per hour – this is a typical figure for a room without mechanical ventilation. Table 5 shows the effect of increasing the ventilation to 1 air change an hour.

c. **Spillage:** Table 6 shows that spillage can have a dramatic effect on oxygen levels. For these calculations the effect of ventilation was ignored. Further assumptions are that the LN vaporises immediately and the released nitrogen gas mixes with the air. The figures therefore represent a pessimistic case.

Table 4: Oxygen concentration, %: effect of topping-up with 10litres LN + evaporation; 0.4 air changes/hour

Room volume m^3	**Volume of Liquid Nitrogen,liter**										
	10	25	50	75	100	150	200	250	300	400	500
15	18.6	18.6	18.5	18.5	18.5	18.4	18.3	18.2	18.1	18.0	17.8
25	19.6	19.5	19.5	19.5	19.5	19.4	19.4	19.3	19.3	19.2	19.1
50	20.3	20.3	20.3	20.2	20.2	20.2	20.2	20.2	20.1	20.1	20.0
75	20.5	20.5	20.5	20.5	20.5	20.5	20.4	20.4	20.4	20.4	20.3
100	20.6	20.6	20.6	20.6	20.6	20.6	20.6	20.6	20.6	20.5	20.5

Table 5: Oxygen concentration, % effect of topping-up with 10litres LN + evaporation; 1 air change/hour

Room volume m^3	**Volume of Liquid Nitrogen,liter**										
	10	25	50	75	100	150	200	250	300	400	500
15	20.0	20.0	20.0	20.0	20.0	19.9	19.9	19.9	19.9	19.8	19.7
25	20.4	20.4	20.4	20.4	20.4	20.4	20.3	20.3	20.3	20.3	20.2
50	20.7	20.7	20.7	20.7	20.7	20.7	20.7	20.7	20.7	20.6	20.6
75	20.8	20.8	20.8	20.8	20.8	20.8	20.8	20.8	20.8	20.7	20.7
100	20.9	20.9	20.9	20.8	20.8	20.8	20.8	20.8	20.8	20.8	20.8

Table 6: Oxygen concentration, %: effect of spillage

Room volume m³	Volume of liquid nitrogen spilled, litres						
	1	2	3	4	5	10	25
15	19.6	18.1	16.7	15.3	13.8	6.7	
25	20.4	19.9	19.3	18.7	18.1	15.3	
50	20.7	20.4	20.1	19.9	19.6	18.1	
75	20.8	20.6	20.4	20.2	20.0	19.1	16.2
100	20.9	20.7	20.6	20.4	20.3	19.6	17.4

On table 3, it is shown that if the room is medium level ventilated, there is no serious health problem arises in case of presence of storage containers. However, comparison of Table 3 and 4 shows that how the small amount of liquid nitrogen, as 10 liter, changes the structure of the air dramatically. On the other hand, it is given in Table 5, how the ventilation eliminates the hazards.

In Table 6, the effect of the spillage of the liquid nitrogen in the places where no ventilation present.

Do not store liquid nitrogen and work with liquid nitrogen in places where the ventilation is poor.If you are not sure that there is sufficient oxygen in the room, do not enter the room without personel protective equipment. Throughly venilate the room.

Cold Burn: Exposure of the skin to a cryogenic liquid or its cold vapour/gas can produce skin burns similar to heat burns. The severity of a cold burn depends on the temperature and the time of exposure. Even brief contact with cryogenic fluids can cause cold burns.

If there is a risk of contact with cryogenic liquids, use personel protective equipment

Hypothermia: Exposure to low air temperatures can cause hypothermia. Hypothermia is a condition associated to the decrease of body temperature below 35 °C. The susceptibility of a person to hypothermia depends on the temperature, the exposure time and the person's physical conditions (older people are more likely to succumb). Typical symptoms of hypothermia are mild to strong shivering, muscle misFcoordination, inability to use hands, stumbling, mild confusion, difficulty in speaking and amnesia. When the body temperature goes below 33 °C the victim could get unconscious or asleep and after some time could fall into coma[2].

Effect of cold on lungs: Patients suffering from bronchial asthma or chronic obstructive lung diseases often experience aggravation of bronchospasm on exposure to cold environment. Inhalation of cold mist, gases or vapours from the evaporation of cryogenic liquids worsens the degree of airway obstruction for sensitive patients. Short exposure creates discomfort even in normal subjects and could damage the lungs in case of prolonged exposure

Contact with cold surfaces: If unprotected skin comes into contact with cold surfaces, like noninsulated pipes or vessels, the skin may stick and flesh may be torn off on removal.

Toxicity: Although Nitrogen is a nontoxic gas, this manul includes general information about toxicity of cryogens. Ozone (O_3), carbon monoxide (CO) and fluorine (F_2) are highly toxic. Exposure to concentrations of ozone in excess of several tenths of a ppm can cause headaches, dryness of the throat and of the mucous membranes of eyes and nose. At a concentration of 1 ppm O_3 is a strong irritant to the respiratory system and eyes. Exposure to concentrations exceeding 2 ppm over several hours produces effects on the lung characterized by pulmonary congestion. The maximum permissible O_3 concentration is 0.1 ppm. It is worth to mention that ozone besides being extremely toxic also presents an explosive hazard. Liquid ozone can decompose explosively when heated by a heat source or by chemical reaction with reducing agents. A small ignition source like a spark or a fast warming above its normal boiling point temperature (161 K) can cause detonation.

Carbon monoxide is hazardous if inhaled. CO can combine with haemoglobin in the blood making it incapable of carrying oxygen to body tissues. Symptoms depend on the CO concentration and time of exposure. Exposure to CO for halfFhour at a concentration of 1000-2000 ppm produces slight heart palpitations and headache, nausea might be experienced after two hours of exposure. Inhalation of a concentration of 4000 ppm can be fatal in less than one hour. The maximum permissible CO concentration is 30 ppm.

1.2. FIRST AID

Asphyxiation: Person suffering from lack of oxygen should be moved to fresh air. If a victim has stopped breathing then immediately apply artificial respiration. If breathing is difficult supply extra oxygen. Arrange medical attention as soon as possible. Do not try to help the victim without the person moved to fresh air. Otherwise you may be a second victim.

Contact with skin: In case of contact with cryogenic liquids, the clothes which prevent air circulation of the contacted region shall be removed immediately. Do not scrub the freezed body parts. Wash the exposed region by water not exceeding 40°C. Never apply dry hot.

Cold Burn: In case of cold burn, while waiting for the medical help, flush with copious amounts of tepid water or immerge the affected area in a warm water at room temperature. Do

not rub or massage the affected area. Cover the affected area with sterile dry dressing to protect from infection. The bandage should be loose and should not restrict blood circulation.

Hypothermia: If you suspect hypotermia, to protect internal organs, move the victim to a warm place. Wrap the victim in blankets or several layers of clothes to keep warm. o not use direct forms of heating to warm (radiators or fires).

Contact with eye: In case of contact of cryogenic liquid or extremely cold gas with eyeFlush eyes immediately with warm water not exceeding 40°C. Use preferably the eye shower and rinse for at least 15 minutes. Arrange medical attention as soon as possible.

2. SAFETY

2.1. PERSONAL SAFETY

The users of liquid nitrogen should use personel protective equipment.

Cryogenic gloves: Wear cryogenic gloves for the spillage risk of cryogenics. Use large size to allow quick removal.

Face shield: To protect your face wear face shield or safety glasses.

Additionaly, Wear clothes with long sleeves and a lab coat, long trousers and closed shoes. Do not work by wet clothes. All of the equipment, tools and clothes should be oil free.

2.2. ADDITIONAL SAFETY PRECAUTIONS

- Do not allow untrained people to work with cryogenic liquids.
- Keep close the MSDS of the cryogenic liquid that you use.
- Never use contact lens while working with cryogenic liquids.
- Do not ever make a media transfer in the places where accumulation could be evacuated in dangerous amounts.
- Do not touch any material unless you sure that it is at room temperature.
- Be carefull during transfer of liquid nitrogen to prevent splash and fast cooling of the container.
- Do not allow untrained people to do maintanace to the equipment in use.
- Read the related documents thoroughly before using your system.

Ventilation of the Room:

Large quantities of cryogenic liquids must be stored in open air or in well ventilated areas. Small and unventilated rooms should be avoided because gas would accumulate in these rooms as the liquid cryogen evaporates. A well ventilated laboratory has a number of air changes per hour between 5 and 10. Taking into consideration, to prevent oxygen depletion the places where the personel worked should be used high flow ventilation

If it is not possible;

- There should be at least two oxygen depletion sensor and alarm system.
- The voice of alarm must be heard from out of the room.
- The malfunctions in alarm system must be seen/heard from the outside of the room.
- When deciding where to position the monitor, consideration should be given to type of the gas that the risk of asphyxia resulted from. For lighter than air gases, such as He,N_2, the unit should be positioned above the head (approx.2m). For heavier than air liquids and gases such as liquid Nitrogen, the unit should be positioned approximataly 1 meter above from floor. If it is positioned below, the unit will give alarm among each nitrogen transfer.
- Dedectors should provide time to person in an emergency case for asking for help. Before the installation, contact should be supplied with supplier.
- Dedector and alarm systems should be energized considering the power cut and their maintanence should be done periodically.

3. USAGE AND STORAGE

Follow the rules given in section 3. Always use protective equipment. The user should be trained on the material properties which is exposed to cold. To prevent gas expansion, cryogenic liquids should be stored in adequate ventilated rooms.

Most of the materials have different properties in extremely low temperatures than normal temperatures. Do not use materials that you don't know low temperature properties in these temperatures.

3.1. TRANSPORTATION

Transport liquefied gases in suitable, insulated containers that provide means for the escape of gas as liquid evaporates. Never cork or plug the outlet of such containers. The containers should be tested and labelled suitable for the cryogenic liquid.

Pay attention to the following items while carrying portable containers and dewars

- Plan the route in advance.

- Be aware of your physical capabilities, some cylinders are heavy and need more than one person to be displaced. Plan rest stops if necessary. Avoid moving the cylinder through populated work areas.
- Be aware of possible clutter and obstructions. Check the floor is solid and even.
- Prefer lifts to stairs when moving cylinders with capacities of several liters. Do not use lifts with liquid nitrogen containers.
- Do not attempt to catch a cylinder or flask if it falls.

3.2. STORAGE

Storage of cryogenic liquids should be done by trained and experienced people.

Liquid Nitrogen Storage Containers

• There are three types of containers: Dewar, Cryogenic Liquid Cylinder, and Cryogenic Storage Tank. Storage varies from a few liters to thousands. Vaporization is always continuous. This is because heat leaks are always present.

Dewar: Non pressurized containers. Typical capacity is a liter. Product may be removed to smaller containers by pouring, but larger sizes require a transfer tube. A loose fitting dust cap over the outlet prevents moisture from plugging the vent, allowing gas to escape.

Cryogenic Liquid Cylinder: Cryogenic liquid cylinders are, Insulated, vacuum jacketed pressure vessels. They operate up to 350 psi and have capacities between 80-450 L. Product may be withdrawn as a gas by passing through an internal vaporizer or as a liquid under its own vapor pressure. They become equipped with safety relief valves and rupture discs. This protects from pressure build up.

Cryogenic Storage Tanks: Typically includes a tank, a vaporizer, and a pressure control manifold. Cryogenic storage tanks may be spherical or cylindrical in shape. Their sizes range from 500-420,000 gallons. They are powder and vacuum insulated [4].

When storing pressurised cylinders and nonpressurised dewars it is advised to follow few basic rules: :

• Use only cylinders and dewars proper to store cryogens.

• Store the cylinder/dewar below 50 oC and in a wellFventilated place.

- Vents and openings must be oriented away from personnel and lab equipment.
- Do not store cylinders and dewars on stairwells.
- Do not store cryogenic liquids with corrosive or flammable chemicals.
- Ensure appropriate hazard warning signs are displayed.

3.3. LIQUID NITROGEN TRANSFER

Liquid Nitrogen transfer is dangerous !

Risks of Asphyxiation and unconsciousness !

Transfer Line: Transfer lines are used to remove liquid from Dewar or cryogenic liquid storage containers. Cryogenic lines are always connected to the cylinder's liquid withdrawal valve. Use only transfer lines designed for cryogenic equipment [3].

Gas withdrawal: To prevent back contamination, all valves should be closed when the container has been emptied.

Liquid withdrawal: Always wear a face mask for liquid withdrawal. Connect a transfer line from the liquid valve to the system being filled. Open valve to desired rate of flow, close when finished. To prevent back contamination, all valves should be closed when the container has been emptied.

Some general basic rules must be followed when transferring cryogenic liquid from one container to another is given below:

- Use only proper transfer equipment. Remember that transfer lines must be regularly checked. Vacuum insulated transfer lines must be purged every few months, check the instruction manual of the manufacturer to know how often your transfer line needs to be purged.
- Ensure cylinders and dewars are adequate for the cryogen you use and are clearly labelled.
- Wear personal protective equipment. It is recommended to wear cryogenic gloves, glasses, goggles or a facemask and a lab coat or apron. Wear closed or work shoes. Open shoes or shoes of porous material such as fabric are not allowed.

- Ensure the receiving vessel is clean and dry to avoid ice to form at the bottom of the vessel.
- Do not leave vessels unattended while filling them.
- Before filling a receiving vessel cool it down by adding a little cryogenic liquid first.
- Do not allow the cryogenic liquid to fall through a distance to reach the receiving vessel.
- When manually pouring liquid into a smaller dewar, ensure that the latter is secured and cannot tip over while filling it.
- Dispense cryogenic liquids slowly into the receiving vessel to minimize splashing, spillage[2]

REFERENCES

1. Safe Use of Liquid Nitrogen, Royal Free Hampstead NHS Trust& Royal Free & University College Medical School, 2004
2. Cryogenic Safety Manual, EPFL SB-SST,December 2012
3. *Liquid Nitrogen Safety Presentation, Ohio University, Retrieved on: 07 Aralık 2015 ohio.edu>riskandsafety>docs>liquidnitrogensafety*
4. *Retrieved on 2015, December 07,from https://rgs.usu.edu>uploads>lab-safety*