C07 Safe Handling of Cryogens

1. Introduction

Cryogens (Cryogenic liquids) are frequently used in the laboratories for operation of specific equipment, freezing of foods and preservation of biological samples. Cryogens should be handled with extreme care as they are extremely cold and can be converted into gases at very high rate posing various hazards. The purpose of this document is to provide laboratory personnel at the Science Park with general guidelines on safe handling, transport and storage of cryogens in the laboratories.

2. Definition

Cryogens are liquefied gases that are kept in their liquid state at very low temperature. These liquids typically have boiling points below -150°C and are gases at normal room temperature and atmosphere pressure. Most cryogenic liquids are odorless, colorless (except for liquid oxygen which is light blue) and tasteless when vaporized into the gaseous state. Cryogens must be stored, shipped and handled in special designed containers. The hazards associated with cryogens arise from their extremely low temperature, pressure building up in the containers and high expansion rate to gases when discharging.

3. Types of Cryogens

Cryogens can be classified into the following three groups. Each has its own unique properties.

3.1 Inert Gases

These gases do not react chemically to any great extent, nor burn and support combustion. Examples of this group include nitrogen, argon, helium and neon.

3.2 Flammable Gases

Some cryogens when vaporized can burn in air. The most common examples are hydrogen, methane and liquefied natural gas.

3.3 Oxygen

Liquefied oxygen is a very powerful oxidizing agent and can burn rapidly or react explosively with organic materials. Many materials considered as non-combustible can also burn in the presence of oxygen.

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4. Cryogen Containers

A cryogenic liquid cannot be indefinitely maintained as a liquid, even in a well-insulated container. Vapor generated produces enormous pressure that could rupture the container. Thus, cryogen containers are normally equipped with pressure relief valve for primary protection and rupture disc for secondary protection. The types of containers for cryogen include dewar, cryogenic liquid cylinder and cryogenic storage tank. All containers should be clearly labeled and operated in accordance with manufacturer's instructions.

4.1 Dewar

Dewar flasks are non-pressurized, vacuum jacketed vessels, somewhat like a "Thermos bottle". They should have a loose fitting cap or plug that prevents air and moisture from entering and allows excessive pressure to vent. The capacity of a dewar flask ranges from 5 to 200 liters.

4.2 Cryogenic Liquid Cylinder

Cryogenic liquid cylinders are insulated, vacuum jacketed and pressurized vessels. They have valves for filling and dispensing the cryogenic liquid, and a pressure control valve with a rupture disk to protect the cylinders from excessive pressure buildup. These containers operate at pressure up to 350 psi and have capacities between 80 and 450 liters of liquid.

4.3 Cryogenic Storage Tank

A cryogenic storage tank is usually mounted in fixed location as stationary vessel or on truck for easy transportation. It contains a tank, vaporizer and pressure control manifold. Tanks are equipped with various circuits to control product fill, pressure buildup, pressure relief, product withdrawal and tank vacuum. The size of the tanks ranges from 500 to 420000 gallon.

5. Hazards Associated with Cryogens

Cryogens can be hazardous to laboratory personnel or cause damage to properties if they are not handled properly.

5.1 Skin and Eye Hazard

The high expansion ratio property makes cryogen more prone to splash, and therefore may damage skin and eye. Cryogens are extremely cold which cause instant and severe frostbite. Direct contact with cryogenic liquids, uninsulated cryogenic pipes or equipment can cause freeze burns and tissue damage.

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5.2 Cold Embrittlement

At cryogenic temperature many materials such as rubber, plastic and carbon steel can become so brittle that very little stress can break the materials. Avoid using these materials for handling of cryogens. Do not dispose cryogenic liquids down the drain as polyvinyl chloride (PVC) piping in laboratory sinks may not be able to resist cryogenic temperature.

5.3 Asphyxiation

The accidental release of inert cryogenic liquids will quickly transfer to gaseous phase and displace the oxygen content of the surrounding area. This will cause asphyxiation hazard to personnel working in the area. Oxygen detectors are recommended in some confined and poorly ventilated areas. Personnel should not be permitted in atmospheres containing less than 19.5% oxygen without supplied air.

5.4 Explosion due to Rapid Expansion

Without adequate venting or pressure relief devices on the containers, enormous pressure can build up. The pressure can cause an explosion called a “boiling liquid expanding vapour explosion’ (BLEVE). Accidental conditions such as an external fire, or a break in the vacuum which provides thermal insulation, may cause a very rapid pressure rise. The pressure relief valve are unable to handle this increased pressure, thus, rupture disc is installed for secondary protection.

5.5 Fire

Flammable gases such as hydrogen, methane, carbon monoxide and liquefied natural gas can burn and explode. It should be kept away from any ignition source. Hydrogen is particularly hazardous which can form flammable mixtures with air over a wide range of concentration (4-75% v/v) and very easily ignited.

5.6 Toxic

The toxic hazard of a particular cryogen should be identified by referring to the Material Safety Data Sheet. For example, the release of large quantities of carbon monoxide can cause death almost immediately.

5.7 Oxygen Enrichment

When transferring liquid nitrogen through uninsulated metal pipes, the air surrounding a cryogen containment system can condense. Nitrogen evaporates more rapidly than oxygen. This can leave an oxygen-enriched condensate on the surface that can increase the combustibility of materials near the system. Equipment

containing cryogens must be kept clear of combustible materials in order to minimize the fire hazard potential.

6. Personal Protective Equipment

6.1 Eye and Face Protection

Full face shield and splash resistance goggles provide the best protection for the eyes and face. Safety glasses cannot protect the face entirely and contact lens should not be worn.

6.2 Hand Protection (Gloves)

Always wear appropriate cryogenic gloves, such as loose-fitting thermal insulated or leather gloves. Gloves should be loose-fitting so they are able to be quickly removed if cryogenic liquid is spilled on them. Rubber gloves should not be used because they could harden instantly.

6.3 Proper Clothing and Shoes

Wear closed-toe shoes or safety shoes, along with lab coat or long sleeve shirt and trousers without cuffs, when handling cryogens.

7. Handling, Transfer and Storage of Cryogens

All laboratory operators at the Science Park are required to comply with the Dangerous Goods Ordinance (CAP. 295) on handling and storage of cryogens. Cryogen (Liquefied gases) are classified as Category 2, Class 2 in the Ordinance.

7.1 Handling of Cryogens

Some general practices are described below:

a) Standard operating procedures are developed for specific operations on different cryogens.
b) Laboratory personnel working with the cryogens are well trained and familiar with the standard operating procedures.
c) For particular hazardous operation, a work permit system should be put into place. A competent person should examine all the equipment and review the proposed procedures before the work begins.
d) Identify the hazard potential of the cryogen and wear appropriate personal protective equipment accordingly.

e) Advise to remove all the metal watches, rings, bracelets before working with cryogens. If exposed to cryogens or boil-off gases, they can freeze to the skin.
f) Ensure all equipment and containers are free of oil, grease, dirt or other materials which may lead to fire hazard.
g) Do not allow water to contaminate the equipment as freezing water will expand and may cause equipment cracking.
h) Conduct operations in well ventilated areas or with local exhaust ventilation to prevent possible gas or vapor accumulation.
i) Never allow any unprotected part of body to contact with uninsulated pipes or vessels which contain cryogens.
j) When using cryogenic liquid to cool an object, insert the object slowly using tongs.
k) Ensure containers are properly labeled with the identity of the cryogen. Do not mix different cryogens into the same containers.
l) Never pour cryogenic liquids into any drain.

7.2 Transfer of Cryogens

Some general practices are described below:

a) Transfer or pour cryogens slowly to minimize boiling and splashing. Use a special filling funnel (the top of the funnel should be partly covered). If the liquid cannot be poured, use a cryogenic liquid withdrawal device for transfer.
b) When transfer to secondary container, slowly fill the container not more than 80% of its capacity.
c) Never roll, drag or drop containers or permit them to strike each other.
d) Use suitable hand truck or cart for cryogenic liquid container movement. Use a strap to secure the container to the hand truck or cart.
e) If cryogens must be transported by elevator, ensure that no passengers get on the elevator while the cryogen is being transported.

7.3 Storage of Cryogens

Cryogens shall not be stored in the laboratories in excess of their respective exempt quantities or the aggregated quantities specified in the Ordinance. The excessive cryogens should be stored in HKSTP's Central Dangerous Goods Stores. The following safety measures should be adhered to regarding storage of cryogens:

a) Keep cryogen containers upright in cool and well ventilated areas, away from incompatible materials and ignition sources.
b) As far as reasonably practicable, install oxygen or flammable gas monitor systems in appropriate areas for continuous monitoring.
c) Use only approved storage containers equipped with protection devices.

d) Avoid the contact of moisture with storage containers to prevent ice plugs in relief devices.
e) Do not store cryogen containers on hand carts as they could fall or get knocked over.
f) Provide adequate access for handling cryogen containers.
g) Visually inspect stored cryogen containers on a routine basis for any indication of leakage or damage.

8. Emergency

Laboratory Persons In-Charge should address the potential hazards of cryogens and the corresponding safety measures to all concerned laboratory personnel. In the event of skin contact, eye exposure or cryogens leakage, follow the emergency procedures listed below:

8.1 Skin Contact

a) Remove any clothing that may restrict blood circulation to frozen area.
b) Do not rub the affected part of the body. Rubbing may further damage the tissue.
c) Rinse the affected area with warm water (<40°C) for 15 minutes to gradually warm up the affected area.
d) Seek medical attention immediately.

8.2 Eye Exposure

a) Flush the eyes with warm water (<40°C) for 15 minutes.
b) Seek medical attention immediately.

8.3 Cryogens leakage

a) Alert other people and evacuate the area immediately.
b) Ventilate the area by opening the windows or activate the emergency ventilation or any forced ventilation to allow any split liquid to evaporate and the resultant gas to disperse.
c) Report the incident to HKSTP following the “General Laboratory Emergency Procedures” in the SHE Handbook.
d) The laboratory should be cordoned off and warning signs should be posted on the exits. Do not re-enter the area until it is clear of cryogens.