Chemical Safety Guidance

February 2020

Reduced Oxygen Atmospheres: Resulting from the Use of Cryogens or Compressed Gases in the Workplace

Occupational Health and Safety Service
HSD053C (rev4)

UNIVERSITY OF CAMBRIDGE

Reduced Oxygen Atmospheres Resulting from the Use of Cryogens or Compressed Gases in the Workplace

1. Introduction

The air we breathe normally contains approximately 78% nitrogen, 20.9% oxygen, 0.93% argon, 0.04% carbon dioxide, and trace amounts of other gases, in addition to water vapour.

Oxygen is the only gas that supports life and its concentration in the workplace should be maintained above 19.5% through adequate ventilation and the control of other gases introduced into the workplace.

Working in a reduced oxygen atmosphere below 19.5% is not permitted within the University.

Working in a reduced oxygen atmosphere below 18% can result in dizziness and potentially loss of consciousness. Attempting to work in even lower oxygen concentrations can result in severe brain damage and DEATH.

It should also be noted that working in any oxygen enriched atmosphere is potentially dangerous due to the substantially increased risk of fire and working in an atmosphere above 23% oxygen is not permitted in the University. Note: Nitrogen generators are at least capable of increasing the oxygen level, particularly in small unventilated rooms, this possibility should be risk assessed based on a calculation of amount of nitrogen removed.

2. General

Oxygen reduced atmospheres can result by gas release from:

- Cryogenic liquid tanks / vessels / dewars / flasks by
  - normal evaporation in a confined or unventilated space
  - spillage whilst decanting or if a dewar is tipped over
  - faulty pipe work, faulty valves or even valves left ‘open’
  - pressure relief valves from pressurised containers / tanks

Note: 1 litre of liquid nitrogen produces ~680 litres of gas at room temperature (see Appendix 1).

- Dry ice - release of carbon dioxide gas by sublimation from the solid form.

  Note: **1 kg of dry ice produces 540 litres** of carbon dioxide gas (dry ice has a density of ~ 1.5). Therefore 10 kg in an average cold room could reduce the oxygen level below 15%, **however in doing so would also create a potentially lethal concentration of carbon dioxide** †

- Release from normal use of a gas
  - Welding
  - Purging
  - Chilling and freezing operations
  - Gas blanketing
  - Gas combustion products, this may also release hazardous gases such as carbon monoxide and complex hydrocarbons.
- leaks from pipework regulators or cylinders, see the University’s guidance on the use of compressed gases available on the Safety Office website
- quenching, for example from NMR or MRI
- ‘stale air’ in a confined space ie: pit, tunnel, vessel, duct, tank or bin
- Other means………….

† At concentrations between 2 and 10%, carbon dioxide causes an increased respiratory rate, nausea, dizziness, headache, mental confusion and increased blood pressure. If the carbon dioxide concentration rises above 10% suffocation and death can occur in minutes.
The Health and Safety Executive’s Workplace Exposure Limit (WEL) for carbon dioxide is 5,000 ppm (0.5%) for 8 hours (TWA) or 15000 ppm (1.5%) for 15 minutes (TWA).

Carbon Dioxide is NOT a simple asphixiant BUT is effectively a poisonous gas!

In addition to the use of dry ice (solid carbon dioxide), liquid carbon dioxide tanks are increasingly being used to supply carbon dioxide gas to incubators in laboratories. The use of these large carbon dioxide gas supplies needs careful risk assessment with appropriate monitoring and control measures. **These large liquid carbon dioxide tanks represent a very substantial potential risk**. In addition the liquid derived gas supplies to laboratories MUST be based on robust metal pipework distribution systems appropriate for the gas.

3. Hazards Associated with Oxygen Depletion.

The figures in the table below represent a rough guide of the potential hazardous effects of oxygen depletion on 'healthy' individuals. However, those with lung, breathing or other health problems could experience the effects sooner (i.e. at higher oxygen levels), and could be more severely affected than 'healthy' individuals.

Oxygen Level		**ACTION**
20.9 %	**Normal / No ill effects**	**None**
19.5 %	**Workplace Minimum** (BCGA GN11) activation level of most oxygen monitors	**Risk Assess**
18 %	**Critical Action Level – ACTIONS REQUIRED** Atmospheres containing less than 18% oxygen are potentially dangerous due to a progressively increasing risk of asphyxiation and death.	Entry into areas below 18% should be prohibited*.
12 %	**DANGER of DEATH** **Oxygen levels of less than 12% can cause sudden loss of consciousness - without any warning**** - **followed by or DEATH or severe brain damage, even if rescue and resuscitation is immediate!**	Entry into areas below 12% must be absolutely prohibited to all but the Emergency Services.
10 % to 0	**Even a single breath at oxygen concentrations below 10% can result in loss of consciousness - and DEATH may follow**	

* To all but trained, suitably equipped and competent persons using Breathing Apparatus, i.e. members of the Emergency Services.

** In very low oxygen environments the lungs actually give up oxygen to the air, rather than taking it in. Therefore if an individual were to take a breath at such a low level it will result in a **loss of oxygen from the blood stream!**

4. Risk Assessment

Risk assessment should initially consider the worst case scenario for a particular location, ie: the maximum possible release of gas from the given source instantaneously into the unventilated area. The level of potential oxygen depletion can then be determined by a fairly simple calculation; see BCGA GN11 or use the University's online oxygen depletion calculator at:

http://www.safety.admin.cam.ac.uk/subjects/chemicals/gas-and-oxygen-depletion-calculator

However this simple calculation does not make allowances for:

- furniture and equipment that will reduce the air volume in the room
- the lack of instantaneous diffusion through an area, **which could result in localised high levels of asphyxiant**, nor
- the dilution effects of ventilation, whether natural or forced.

If this crude calculation indicates that **without ventilation** the oxygen level could fall below 19.5%, then the risk assessment should consider a number of factors in detail, including:

- the possibility and probability of an instantaneous release of all the gas
    - by damage, tipping or failure of a vessel
    - by failure of a valve or regulator
    - by failure of a piece of equipment or an experimental rig
    - by any other means
- the possibility and probability of a slow release of all the gas, overnight or over a weekend / holiday period
    - by damage, tipping or failure of a vessel
    - by failure of a valve or regulator
    - by failure of a piece of equipment or an experimental rig
    - by any other means
- the effects of natural (passive) or mechanically forced ventilation on:
    - an instantaneous release of all the gas
    - a slow release of all the gas
- **the potential effects of ventilation failure, including:**
    - **How a user would know the ventilation was functioning or not !**

NB: The 'failure' of a mechanical ventilation system has been directly implicated in at least one fatality arising from an oxygen depleted atmosphere in a research laboratory.

All laboratories should have at least 6 to 8 air changes per hour delivered via mechanical ventilation.

However, when carrying out a risk assessment it must **never** be assumed that an area or laboratory actually has mechanical ventilation, and it must never be automatically assumed that it is functional. If mechanical ventilation of an area is identified in a risk assessment and is thereby used as a control measure, then under the Control of Substances Hazardous to Health Regulations (COSHH) it legally MUST have at least annual inspection and testing to ensure it is delivering the specified level of ventilation (recorded air flow measurements are required), in the same way as a fume cupboard or other local exhaust ventilation system does.

5. Action Matrix for Workplaces Where a Reduced Oxygen Atmosphere Could Arise

	Below 19.5%	**Below 18%**	**Below 12%**
A workplace in which a reduced oxygen atmosphere could be present for long periods or frequently.	VENTILATION & MONITORING MUST BE INSTALLED & MAINTAINED	**NOT PERMITTED**	**NOT PERMITTED**
A workplace in which a reduced oxygen atmosphere could occur occasionally for **short periods** as part of normal operations.	VENTILATION and CONSIDER MONITORING IN THE RISK ASSESSMENT	VENTILATION and MONITORING MUST BE INSTALLED & MAINTAINED	**NOT PERMITTED**
A workplace in which a reduced oxygen atmosphere is not likely to occur in normal operation; but could occur as a result of an incident or system failure.	VENTILATION	VENTILATION and MONITORING MUST BE INSTALLED & MAINTAINED	VENTILATION and MONITORING‡ MUST BE INSTALLED and MAINTAINED

‡ The risk assessment should consider the use of dual monitoring, both fixed and a personal alarm, if the risk of the oxygen level falling below 12%, as a result of an incident or system failure, is at all significant. In addition the system should be re-evaluated to remove this risk or reduce it as low as reasonably practicable.

This matrix should be used as guidance only in the selection of engineering controls to ensure that the oxygen level in the workplace is maintained above 19.5%.
The final choice must be based upon a realistic Risk Assessment of the task being undertaken and after consideration of all the potential control measures listed below:

6. Engineering Control Measures

Wherever reasonably practicable prevent or reduce the risk by using engineering controls:

- **Reducing the quantity of cryogen or compressed gas in the area / laboratory to the lowest that is reasonably practicable**
  - by use smaller gas cylinders
  - by use smaller cryogen dewars / smaller volumes of cryogen etc.
- correct specification of equipment
- regular inspection of equipment
- regular maintenance of equipment
- external venting of exhausts, pressure relief valves, and quench vent pipes
- correct location and installation of equipment ie: relocate to a safer place
  - do not use gas cylinders or cryogens in unventilated areas
    - wherever possible avoid using rooms below ground level
- locating tanks and gas cylinders outside buildings where practicable
- ensuring there is good visibility into the work area through windows and/or door panels

If the risk assessment identifies that the oxygen concentration could foreseeably fall below 19.5% then monitoring should be used and engineering control measures considered. If the oxygen concentration could fall to less than 18% then oxygen monitoring AND engineering controls must be implemented to reduce the risk as far as reasonably practicable, including:

- **Ventilation** ¥
  - **Natural / Passive**
    - permanently open vents to the outside increase ventilation
    - opening doors and windows - this requires strict management and should not be considered as permanent solution, always better to use -
  - **Forced / Mechanical** ie: extract fans venting to a safe place outside of the building, with visual indicators of operation at the entrance to the area i.e. 'indicator lights' and/or airflow gauges **by the door.**
- **Monitoring** ¥ of the oxygen level by:
  - fixed continuous mains operated monitors are the preferred option, with
    - alarms; audible and visual, **both inside and outside the room**
    - % oxygen readouts, both inside and outside the room
    - battery back-up power supply in the event of mains failure
    - regular maintenance and calibration as per manufacturer's guidance
  - where appropriate, portable 'hand held' personal monitors with
    - alarms; audible and visual
    - % oxygen readouts
    - regular maintenance and calibration as per manufacturer's guidance
    - remember hand held monitors are portable and could be 'misplaced'
- **Signage**
  - alerting anyone entering the area of the danger and what to do if the alarm sounds
  - and alerting anyone in the area of what to do if the alarm sounds (i.e. 'leave')

See the gas and cryogen warning signage templates on the safety office website at:

http://www.safety.admin.cam.ac.uk/publications/hsd053c-reduced-oxygen-atmospheres-resulting-use-cryogens-or-compressed-gases-work

¥ The location of fixed monitors and ventilation ducts should be carefully considered so as to be effective, at the correct height for the gas, but not prone to excessive false alarms (Appendix 2).

NB: Only the Breathing Apparatus (BA) of the emergency services, which has it's own independent air supply i.e. from cylinders of compressed air, offers protection against reduced oxygen atmospheres. Filtering face masks do not offer any protection!

7. Management Control Measures

- **Authorisations**
  - a procedure to restrict certain work / access to authorised persons
- **Safe Operating Procedures** with
  - a written safe system of work, including transport, use and disposal
  - consideration of having a no lone working policy / 'two person buddy system'
  - consideration of a permit to work system for contractors
- **Robust Management**, including a management plan where:
  - named individuals are responsible for key aspects including maintenance and calibration as per manufacturer's guidance
  - all incidents are reported and investigated
  - the system is subject to regular review

- **Information, instruction and training** for those who might be affected, including:
  - hazards of the asphyxiant gases
  - how they are to be used
  - how they should NOT be used or abused
  - precautions required, including personal protective equipment
  - training on area specific hazards
    - especially emergency procedures and first aid
  - an individuals inability to recognise the effects upon themselves

As listed above, the effects of progressive oxygen depletion include, increased breathing volume, accelerated heartbeat, dizziness, increased reaction times, impaired attention, impaired or faulty judgement, impaired coordination, intermittent breathing, rapid fatigue, loss of muscle control, loss of coordination, nausea, vomiting, loss of consciousness, convulsions, brain damage and death. Some of these effects have in the past been confused with 'drunkenness'.
NB: Since the individual does NOT usually realise they are being affected, the effects listed above must NOT be used as any part of a management control strategy in the absence of appropriate engineering controls; excepting the value of these symptoms in educating 'others' as to the potential danger signs in a colleague.

8. Transport

Transport of both compressed gases and cryogens should be subject to risk assessment, strict controls and careful management:

- Gas cylinders should only be transported on appropriate gas cylinder trolleys and
  - appropriate personal protective equipment (PPE) should always be used
  - gas cylinders must never be transported with the regulator still attached
  - consideration must be given to the consequences of the cylinder falling and the valve being damaged, or any eventuality resulting in the cylinder releasing its gas en-route
- **Great care should be taken when moving cryogen dewars**, whether pressurised or non-pressurised, as they usually have small wheels, are often inherently unstable / top heavy and relatively easy to knock over, potentially spilling the contents. Therefore,
  - The transport route should always be checked for any problems before use
  - Large, medium and/or wheeled dewars should never be carried up or down stairs. Small handheld dewars must be subject to rigorous risk assessment for the stairs in question, in particular what would be the consequences of a spill, could it fall through hand rails or would it be contained completely by side walls, how far might it go, what would be the consequences etc?
  - **When lifts are used** they must be 'unoccupied' and subject to rigorous controls
    - only use 'closed' dewars with a low 'standard/normal evaporation rate'. This is the rate at which the cryogen will evaporate naturally from a 'new' dewar and it should be available from the manufacturer, however old/used dewars will often have higher rates, therefore doubling the 'new' rate would be prudent (note: the evaporation rate also varies by cryogen type)
    - Barriers (Tensa-barriers are preferred) and signage should be used to prevent anyone inadvertently riding in the lift with the cryogen dewar.
    - At least two people should be involved, one dispatching the lift and one receiving the lift on the appropriate floors
    - Wherever possible lifts with 'key lock-offs' should be used to prevent the lift being stopped on intervening floors
    - Where a 'key lock-off' is not available it may be necessary to position a 'guardian' on each floor, depending upon the potential access to the lift. This would be especially important in a building with any degree of public access and / or where there may be persons unable to read or understand the signage for language or other reasons.

Cryogens should only be stored in appropriate, labeled, insulating containers; such as dewars specifically manufactured for the purpose for liquids, or robust styrofoam boxes for dry ice.

Do not store dry ice or liquid cryogens in a confined unventilated space, including cold or freezer rooms - which are almost always unventilated

NEVER completely seal a cryogen (liquid or solid) in any container not specifically made to do so. Sealing a cryogen into an airtight container without a pressure relief valve will result in a potentially dangerous build-up of pressure which can result in an explosion (this has occurred with both liquid cryogens and dry ice in UK Universities).

9. Emergency Procedures.

- developing a written emergency plan, which must:
  - be **proportionate to the level of risk**
  - be clear, straight forward and unambiguous, covering
    - evacuation of the danger area**
    - isolation of gas supplies if appropriate
    - safely initiating ventilation of the area
    - alerting responsible persons
    - alerting emergency services if necessary
    - alerting lift engineers to the hazard(s), following a lift breakdown when transporting dewars in a lift (see above)
  - be clearly **understandable by all** who might be called upon to use it
  - **not** expect untrained individuals, such as visitors, ‘passers by’, cleaners, contractors and security guards etc, to carryout actions beyond safely leaving the area and further raising the alarm.
  - include information, instruction, training and **rehearsal**
  - **not place anyone in danger** ⇮

** If an incident requires an evacuation there must be a way of evacuating the area / building without allowing persons to enter or pass through the ‘danger area’. Therefore the ‘fire alarm’ may not be the best choice of alerting occupants to the need to evacuate. The evacuation procedure should be considered in the risk assessment and may involve developing a generic building wide procedure.

⇮ Multiple fatalities have occurred when rescuers have themselves been overcome while attempting to assist an unconscious colleague. The temptation to enter an area to affect a rescue is strong. However, the risks of doing so are extremely high. It is essential that emergency action is planned in advance and that staff are trained to understand the action to be taken in such circumstances. Would-be rescuers MUST NOT attempt to enter an area that contains a dangerously oxygen deficient atmosphere (see section 5. above).

10. SUMMARY of key points:

✓ Calculate the maximum potential release of a gas in the work area and the resultant depletion of oxygen.

✓ If the concentration of oxygen could fall below 19.5% introduce control measures as above.

✓ If monitors are required, they should be mains operated with audible and visible alarms inside and outside of the room.

✓ If mechanical ventilation is required there should be a clear unambiguous indicator at the entrance to the room that the ventilation is functioning.

✓ For more information see sections 1 to 9 above.

FURTHER READING:

British Compressed Gas Association (BGCA) guidance note GN11 (rev3) *Uses of Gases in the Workplace, The Management of Risks Associated with Reduced Oxygen Atmospheres*, 2012. Appendix 1:

Cryogen Data including the Volume of Gas Produced by Evaporating Cryogens

Cryogen	Boiling Point (at 1 atm) °C	Volume of Gas Produced by One Litre of Cryogen	Type of gas
Argon	**- 186**	**850**	**Inert**
Helium	**-269**	**760**	**Inert**
Hydrogen [H]	**-253**	**850**	**Flammable**
Nitrogen	**-196**	**680**	**'Inert'**
Oxygen [O]	**-183**	**860**	**Oxidiser**
Carbon Dioxide [CD] (Dry Ice)	**-78 (a solid that sublimes)**	**540 from 1Kg solid**	**Toxic**

[H] Work with liquid hydrogen is clearly a very high risk activity requiring rigorous risk assessment. Whilst a hydrogen gas release is clearly capable of generating a reduced oxygen atmosphere the greater risk would almost certainly be that of fire or explosion.

[O] Work with liquid oxygen is clearly a very high risk activity requiring rigorous risk assessment. A release of liquid oxygen would increase the oxygen concentration, increasing the risk of fire and potentially causing the spontaneous ignition of any combustible or easily oxidisable materials and even some metals under certain circumstances.

[CD] The storage life of dry ice is affected by the quantity of dry ice, its packing, and storage conditions. Below are some examples of total evaporation times:

- 1 kg at room temperature on a table/bench, approx. 6 - 8 hours
- 10 kg at room temperature in a Styrofoam box, approx. 1 - 2 days
- 20 kg at room temperature in a Styrofoam box, approx. 3 - 4 days

Appendix 2:

Ventilation and Monitors

Ventilation:

The location of ventilation ducts or vents should take into account the relative density of the gas, before mixing, **compared to air at room temperature.** The simple principle being that gases heavier than air require low level vents whilst gases lighter than air generally require high level vents. Gases approximating to the same density as air should be assessed on a case by case basis, allowing for the potential for a gas to cool when being released from a high pressure cylinder (*the Joule-Thomson Effect).* Options include installing vents in the breathing zone (1.5 to 1.8 metres) or to installing both high and low level vents, dependent upon the risk assessment.

Note: Hydrogen, helium and neon exhibit a *Reverse Joule-Thomson Effect*, whereby the gas is heated upon release from high pressure. This can result in the auto-ignition of hydrogen !

There are too many gases in use in the University to attempt to list all their densities here, so the table below only contains data for the 'common' cryogens, further information on gas densities is freely available from suppliers websites.

Cryogens	**Relative Density of evolved gas**	**Ventilation Height**	**Monitor Height**
Argon [a]	1.38	Near floor	30 cm from floor
Helium [a]	0.14	Near ceiling	Near ceiling
Hydrogen [b]	0.07	Near ceiling	Near ceiling
Cryogenic Nitrogen [c]	(0.97)	Near floor [b]	0.5 to 1metre above floor [b]
Oxygen [a]	1.10	Near floor	30 cm from floor
Carbon Dioxide [d]	1.52	Near floor	30 cm from floor

Note:

a. Argon, helium and oxygen would require an oxygen monitor. However helium can cause some oxygen depletion monitors to potentially over-estimate the level of residual oxygen and should be used with caution. When purchasing an oxygen depletion alarm for use with helium the manufacturer's guidance should be sort.

b. All gases except oxygen are potential asphyxiants, however hydrogen is a flammable gas which forms a flammable / explosive atmosphere above a concentration of ~ 4% ie: well before reaching an asphyxiant level. Therefore a hydrogen monitor would be required.

c. Although nitrogen is about the same density as air at room temperature it will be heavier than air when it is cold, ie: when evolving from liquid nitrogen (-196°C). Therefore vents in a liquid nitrogen store would normally be at a low level because the gas would always be very cold as it evolves. Oxygen depletion monitors in a liquid nitrogen store are often fixed at 0.5 to 1 metre as a compromise between the cold nitrogen as it evolves, the warmer nitrogen as it rises and allowing for nitrogen evolution during decanting/filling operations not causing 'false alarms'.

d. Carbon Dioxide from dry ice would be cold. It would be at a toxic level before it could cause asphyxiation, therefore a carbon dioxide monitor would be required.

<u>Monitors / Detectors / Sensors</u>:

Monitoring systems are by their nature safety critical and should be designed and installed by a competent engineer.

Consider the following:

- The most suitable detectors to provide fast and **reliable operation**
- The provision of both fixed monitoring and portable / personal monitoring
  - Personal / portable monitoring only protects if the person with it is present !
  - Given the choice fixed mains alarms are preferred
  - Mains alarms may still need a battery back–up in case of a power failure
- Does the detector / alarm need to be connected to a solenoid shut off valve or similar device to isolate the supply in the event of a leak/release
- The limitations of detectors (i.e. cross-sensitivity to other substances)
- That the detectors must be accessible for testing and maintenance
- That the detectors and cables must be protected against mechanical damage
- That the system will require regular planned maintenance in accordance with manufacturer's guidance

When deciding on the location of sensors a number of factors have to be considered.

- The nature and density of the gas (as evolved and at room temperature)
- The pressure of release, high pressures releases can cause a gas to travel some distance potentially in the breathing zone, before sinking or rising
- The location of the potential source(s)
- Whether the source is mobile
- The relative position of the source and the entrance / exit door(s)
- The size of the room

There is no official figure for the area of coverage a single sensor can be expected to provide, however 50 m^2 per detector is a reasonable maximum, with additional detectors if there are multiple potential sources and/or at points where leakage could occur.

There are no specific standards for gas monitor/detector locations. However there are two general guidance documents (BS EN 50073:1999: Guide for selection, installation, use and maintenance of apparatus for the detection and measurement of combustible gases or oxygen and IEC60079-29-2 Ed1.0: Explosive atmospheres - Part 29-2: Gas detectors - Selection, installation, use and maintenance of detectors for flammable gases and oxygen).

Having considered suitable locations within an area for gas detectors, the mounting height has to be decided. In general, for gases lighter than air the detectors should be above the area where leaks are likely and for gases heavier than air the detectors should be near floor level and in any pits or ducts into which heavy gas may flow. For gases of a similar density to air, the standard practice is to mount the monitors in the 'breathing zone', that is 1.5 to 1.8 metres from the floor, assuming the principle risk is to people standing (this may not be the case i.e. if worker is seated). However, gases do not separate out into discrete layers according to their density, given time they will mix with air and for this reason monitors for cold nitrogen evolving from liquid nitrogen are usually placed between 0.5 and 1 metres from the floor.

When installing gas detectors ensure that the sensor opening is not exposed to liquid or dust contamination by positioning the unit pointing downwards. Spray deflectors should be used when detectors are installed outdoors, or in indoor areas subject to wash-down operations.

Publication history: revised in 2013, 2016 and 2020

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HSD053C (rev 4)