Dangerous Gases Laboratory Standard

This standard is intended to establish the minimum standards required for researchers at Clemson University that utilize dangerous gases as defined below. This standard will help ensure regulatory compliance and the safety of laboratory researchers and building occupants in locations where dangerous gases are used and stored.

Highlights:

- All storage and use of dangerous gases as defined in this standard must be approved by the office of Occupational and Environmental Safety (OES).
- All researchers intending to use dangerous gases must complete a Pre-Operational Safety, Health, and Environmental Review (POSHER) form and submit it to OES for approval.
- All proposals to store and use dangerous gases will be reviewed by university code compliance officials prior to approval.
- The storage, transport, and use of dangerous gases shall comply with all applicable federal, state, and local statutes and in accordance with recognized industry standards.
- Standard Operating Procedures (SOPs) for the use of dangerous gases must be developed by laboratory staff and reviewed / approved by OES.
- Emergency procedures shall be developed by laboratory staff to account for potential gas leaks, fire, explosion, exposures, etc.
- All laboratory workers shall be made aware of the hazards of the gases in use and trained in emergency procedures.
- All dangerous gas cylinders should be located within a ventilated gas cabinet or laboratory fume hood.
- Where necessary gas detection / monitoring systems shall be installed and maintained.
- All work with dangerous gases must also comply with the Clemson Chemical Hygiene Plan and Clemson Laboratory Safety Manual.
- This standard also applies to any dangerous gases that are generated in the lab as part of a chemical synthesis with the intention of capturing and storing the gas (primary product or side product).
- Any inquiries should be directed to the OES Chemical and Laboratory Safety Manger.

Definitions:

Dangerous gas: ***Any gas that may cause significant acute health effects at low concentration***. For purposes of this standard, "dangerous gases" means toxic, highly toxic, corrosive, flammable, and pyrophoric gases with any of the following specific characteristics:

- National Fire Protection Association (NFPA) health hazard rating of 3 or 4;
- NFPA health hazard rating of 2 with poor physiological warning properties;
- Extremely low occupational exposure limits in the absence of an NFPA health rating; or
- Pyrophoric (self-igniting) characteristics.

Pyrophoric, toxic, highly toxic, corrosive, and flammable gases are defined as:

Pyrophoric:
Gas that upon contact with air or oxygen, will ignite spontaneously at or below a temperature of 54.4 °C (130 °F).

Toxic:
Gas with an LC50 in air of more than 200ppm, but not more than 2000ppm by volume of gas or vapor, when administered by continuous inhalation for one hour (or less if death occurs within one hour) to albino rats weighing between 200g and 300g each.

Highly toxic:
Gas with an LC50 in air of 200ppm by volume or less of gas or vapor when administered by continuous inhalation for one hour (or less if death occurs within one hour) to albino rats weighing between 200g and 300g each.

Corrosive:
A gas that causes visible destruction or irreversible alterations in living tissues by chemical action at the site of contact. It may be acidic or alkaline.

Flammable gas: A material which is a gas at 20 °C (68 °F) or less at 14.7 pounds per square inch atmosphere (psia) (101 kPa) of pressure [a material that has a *boiling point* of 20 °C (68 °F) or less at 14.7 psia (101 kPa)] which:

1. Is ignitable at 14.7 psia (101 kPa) when in a mixture of 13 percent or less by volume with air; or
2. Has a flammable range at 14.7 psia (101 kPa) with air of at least 12 percent, regardless of the lower limit.

The limits specified shall be determined at 14.7 psi (101 kPa) of pressure and a temperature of 68 °F (20°C) in accordance with ASTM E 681.

A list of some dangerous gases are listed at the end of this standard.

Dangerous gas review and approval procedure: The storage and use of dangerous gases must be approved by OES prior to acquisition of the gas. It is recommended that OES be contact regarding the intent to use dangerous gases as soon as possible or during preparation of grant proposals, industry contracts, etc. to allow time for review and any facility upgrades (if applicable). The general process for researchers intending to store and use dangerous gases is as follows:

1. Complete and submit a Pre-Operational Safety, Health and Environmental Review (POSHER) form to OES.
2. Complete and submit a Standard Operating Procedure (SOP) for Dangerous Gas Use to OES. This document at a minimum should include the following information:
    a. Gas type / concentration / volume stored in cylinder and temperatures / pressures expected at various points in the process

   b. Apparatus safety features (restricted flow orifice (RFO) size, excess flow valves, shutoff valves, etc.)
   c. Piping material, size, anchorage, and route to be used from cylinder to point of use
   d. Dedicated exhaust used for tool (i.e. certified fume exhaust, gas cabinet, special purpose hood / enclosure, etc.)
   e. Details regarding cylinder installation (i.e. how it will be secured)
   f. Leak check procedures for piping systems prior to opening gas valve and when receiving cylinder(s)
   g. Information regarding monitoring systems and alarms in place
   h. Description of any other collateral hazards (i.e. lasers, electrical)
   i. Each lab should have documentation of cylinder change out procedure as part of the SOP.
   j. Emergency procedures to be implemented in the event of gas leak, fire, explosion, exposure, etc.
3. OES will coordinate a code review, approval, and signoff from the appropriate university and municipal code officials. This may not be necessary for small quantities of a toxic gas in a lecture bottle.
4. OES will coordinate any facility upgrades that may be required for the gas in question.
5. The Executive Director of OES will provide final approval once all safety, code, and infrastructure requirements are met.

Roles and responsibilities: The general roles and responsibilities of interested parties are outlined below. It is the responsibility of each party to ensure the implementation of their outlined responsibilities. Additional roles and responsibilities may be applied as necessary based on the hazards of the gases / processes in use.

Principal Investigator

- Is responsible for ensuring overall safety in the laboratory.
- Develop Standard Operating Procedure (SOP) for dangerous gas storage, transport, and use in the laboratory and ensure all lab members are knowledgeable in its application.
- Ensure the gas inventory is updated with correct names and quantities of dangerous gases.
- Ensure gases are secured and stored properly at all times.
- Check that dangerous gas cylinders received from vendors are equipped with gas tight dust caps on the cylinder gas outlet and cylinder safety caps to protect the gas cylinder valve during transit. All gas cylinders must have the appropriate Department of Transportation (or equivalent) label affixed to the cylinder exterior. If dangerous gas cylinders are received without required cylinder safety caps or labeling, they should not be accepted from the vendor.
- Provide training to all laboratory personnel on the hazards and emergency procedures of the dangerous gases and document training.
- Ensure that laboratory personnel are compliant in following the Clemson Dangerous Gases Laboratory Standard and lab SOP.
- Ensure that required gas monitors are calibrated and replace sensors based on manufacturer specifications. Records must be accessible to OES as part of lab safety reviews. (Note: this may be provided and maintained by the site facility management).
- Ensure operation and maintenance of any dangerous gas engineering controls (i.e. fume hoods, gas cabinets, exhaust snorkels, etc.).

- Notify adjacent labs of dangerous gas use and risks. OES will assist researchers in the coordination and communication about dangerous gas use in the facility.
- Comply with all applicable federal, state, and local ordinances and appropriate recognized industry safety standards.

Laboratory employees

- Review and comply with proper work practices as identified by the approved POSHER, lab specific SOP, PI instructions, and this standard.
- Verify that dangerous gases are always used and stored in properly exhausted enclosures per lab SOPs.
- Understand and properly respond to monitoring alarms.
- Complete all required safety training as directed by the lab PI.
- Fully understand all emergency procedures and use of emergency equipment (i.e. eyewash / safety shower, etc.).
- Utilize all appropriate personnel protective equipment (PPE) as determined by the lab SOP.
- Report any concerns or emergencies promptly to the appropriate parties. OES should be notified of any emergency (i.e. gas leak, fires, exposures, etc.).
- Comply with all general compressed gas safety protocols as outlined in the Clemson Laboratory Safety Manual.
- Do not deviate from approved SOPs. Any alteration to approved SOPs shall be approved by OES.

Occupational and Environmental Safety (OES)

- Assist researchers in safe lab operations utilizing dangerous gases.
- Implement the Clemson Dangerous Gases Laboratory Standard.
- Review and approve a Pre-Operational Safety, Health and Environmental Review (POSHER) form for dangerous gas use.
- Assist code compliance officials in review and approval of dangerous gas use.
- Coordinate facility modifications / upgrades as identified during review process.
- Review and approve dangerous gas delivery system design prior to construction.
- Review and approve dangerous gas SOPs
- Periodically review the lab safety practices for dangerous gas use
- Annually review and update the Clemson Dangerous Gases Laboratory Standard.
- Inform emergency responders (CUFD, CU Police) on dangerous gas locations and emergency response plans for dangerous gas lab spaces.
- Assist in response to alarms related to dangerous gas systems.

General guidance for the use of dangerous gases

Ventilation: Proper ventilation is required in laboratories using dangerous gases. The presence of a fume hood is mandatory unless a gas cabinet and special local exhaust system or filtering system is required. Contact OES to determine if your lab has a ventilation system appropriate for dangerous gas use before purchasing the gas.

Cylinder Size: Use the minimal gas cylinder size possible. For small scale applications, lecture bottle size cylinders are recommended. While the initial purchase cost per cubic foot may be lower when dangerous gases are purchased in full-sized cylinders, the overall cost of experimental setup, which may require local ventilation, gas cabinets, stainless steel piping and purging systems may offset the apparent saving.

Cylinder holders: All compressed gas cylinders, regardless of size, must be properly secured. Use floor or bench clamps or secure gases with chains / straps. A single floor or bench clamp may not be used to secure multiple cylinders unless it is designed for multiple cylinder support.

Regulators: Gases from full-sized gas cylinders must be dispensed using a two-stage regulator, with a diaphragm that is both compatible with the gas and the intended use. A two-stage regulator is a device that reduces the higher pressure in the gas cylinder to a lower working pressure. Two-stage regulators control pressure in two steps allowing precise control of pressure. The maximum pressure of the second stage of the regulator should be as low as is practical for the intended experimental work. Do not select or reuse existing regulators with very high second stage pressure ranges unless needed, since this will require the entire experimental setup (tubing, connections) to be engineered to withstand high pressures. Ensure the proper CGA regulator is selected for the gas in use.

Flow control valves: A mechanical flow control valve (needle valve) that is compatible and properly cleaned for the dangerous gas must be attached directly to the gas out port of the gas regulator. This is required even if other flow control devices are present in the experimental device. Flow control must not be attempted through use of the gas regulator.

Flow restricting orifices: Where feasible, flow restricting devices must be installed after the regulator. Select the appropriate flow restricting device based on gas used and the flow rate required for the research.

Tubing and piping: Dangerous gases must be dispensed using systems that are properly cleaned and compatible with the gas in use. Burst pressure of tubing and piping must exceed the maximum pressure on the second stage regulator. Exceptions to this requirement may be made for short sections of tubing when it and the compressed gas cylinder are completely enclosed in a fume hood and low pressures and flow rates are used.

Purge assembly: Required for all dangerous gas systems that are not used in a fume hood or other ventilated enclosure. Purge assemblies must exhaust into a fume hood or other approved exhaust system. Certain gases may also require purge assemblies within fume hoods or other ventilated enclosures. Exemptions must be approved by OES.

Vacuum pumps: Hydrocarbon based vacuum pump oil is incompatible with strongly oxidizing and many reactive gases. New vacuum pumps that have inert lubricants such as Chemours Krytox® and never contained oil-based lubricants must be used with oxidizing and reactive gases. Vacuum pumps must be securely vented to a fume hood or other approved exhaust system with tubing that is compatible with the gases used. Exhaust lines must be as short as feasible. Vented enclosures may be required for vacuum pumps depending on the toxicity of the gases used.

Leak testing: Hazardous gas systems must be leak tested using inert gas and leak detection solutions such as Snoop® before use. Helium leak testing for all lines conveying highly toxic gases may also be required.

Designated area: The door sign for the laboratory must contain an identifier where dangerous gases are used or stored. All locations within the laboratory where dangerous gases are handled should be demarcated and / or posted with designated area caution signs.

Safety shielding: Safety shielding is required any time there is a risk of explosion, splash hazard, or a highly exothermic reaction. All manipulations of dangerous gases which pose this risk should occur in a fume hood with the sash in the lowest feasible position. Portable shields, which provide protection to all laboratory occupants, are acceptable.

Eyewash and Safety shower: An eyewash and safety shower must be available where dangerous gases are stored / used. Eyewash and safety showers shall be checked for proper function according to the Clemson Laboratory Safety Manual guidance.

Dangerous gas storage:

All dangerous gas cylinders should be located within a ventilated gas cabinet or laboratory fume hood. Ventilated cabinets must meet the following requirements:

- Located in a room or area which has independent exhaust ventilation
- Operate at negative pressure in relation to the surrounding area
- Have self-closing limited access ports or noncombustible windows to provide access to equipment controls, with an average face velocity of at least 200fpm and with a minimum of 150fpm at any part of the access port or window
- Connected to an independent exhaust system
- Have self-closing doors and are constructed of at least 0.097 inch (12 gauge) steel
- Internally sprinklered, (if required), with an appropriate suppression agent
- Anchored securely
- Contain no more than 3 compatible dangerous gas cylinders per gas cabinet unless cylinder contains less than 1 lb of net contents
- All cylinders, regardless of size, must be properly secured within the cabinet or hood

Manipulation of highly toxic and dangerous gases outside of a fume hood, gas cabinet, or exhausted enclosure will require prior OES approval and special ventilation controls in order to minimize exposure. If your research does not permit the handing of dangerous gases in an approved fume hood, gas cabinet, or exhausted enclosure, you must contact the OES to review the adequacy of the ventilation.

Storage and use areas should be secured against unauthorized entry. All exterior storage of dangerous gases must be approved by OES and the Clemson code compliance officer.

All empty dangerous gas cylinders should be labeled as “Empty” and be returned to the vendor. If a vendor will not accept a cylinder or an older or compromised cylinder is found, contact OES for an assessment and to arrange disposal.

Gas detection systems:

Continuous monitoring devices which will alert staff of a release of the dangerous gas are required for certain gases. OES has developed a written Gas Monitoring Program for reference. The detection system should initiate a local visual and audible alarm and where possible transmit a signal to a constantly attended location.

Activation of the monitoring system should automatically close the emergency shut-off valve on dangerous gas supply lines to the system being monitored. Gas monitoring sensor ports should be located inside the ventilated cabinet, near the equipment, and in the lab operator area. An alarm status and gas concentration read out should be located outside the gas use room or be visible through a window. Gas detection may also be necessary to monitor exhaust flow rates, excess gas flow rates, and other controls as defined by code or safe practice. Refer to the Clemson University Gas Monitoring Document for further information on Gas Detection and Monitoring requirements.

Emergency power:

Emergency power should be provided for exhaust ventilation, gas detection systems, emergency alarm systems and temperature control systems. In the event of a power failure, the detection system should continue to operate without interruption or gas systems should automatically shut down at the source. Contingency plans should be developed to address failure of emergency power systems.

Emergency procedures:

Emergency procedures that address response actions to gas leaks, fires, explosions, spills, injury / exposure to staff, or the development of signs and symptoms of overexposure must be developed. All users, lab occupants, and emergency responders should be trained and know how to respond in the event of an emergency. At a minimum, the procedures should address the following at a minimum:

1. Who to contact: (Clemson Fire Department, Clemson Police, OES, Principal Investigator of the laboratory, etc.). Contact information for relevant parties should be posted on the laboratory door sign and known to all lab members.
2. The location and proper use of all safety equipment (showers, eye wash, fire extinguishers, etc.).
3. The method used to alert personnel in nearby areas of potential hazards.
4. The response procedure to any alarm systems that are utilized.
5. Special first aid treatment required by the type of highly toxic material(s) handled in the laboratory (i.e. hydrogen fluoride).
6. Location of gas location(s) (i.e. lab layout), SOPs, safety data sheets, and other information specific to the gases / process should be indicated and available without having to access the lab space.
7. Any other relevant information as it pertains to the specific gases in use.

References:

- South Carolina Fire Code, 2018 Ed.
- NFPA 1
- NFPA 45
- NFPA 55
- NFPA 704
- ANSI/CGA-G-13 – 2016 Ed. (American National Standards Institute / Compressed Gas Association) – Storage and Handling of Silane and Silane Mixtures
- CGA Handbook of Compressed Gases, 4th Ed.

List of Common Dangerous Gases (CAS#) - not comprehensive

Ammonia (7664-41-7)
Arsenic pentafluoride (7784-36-3)
Arsine (7784-42-1)
Boron Tribromide (10294-33-4)
Boron Trichloride (10294-34-5)
Boron Trifluoride (7637-07-2)
Bromine (7726-95-6)
Bromine pentafluoride (7789-30-2)
Bromine trifluoride (7787-71-5)
1,3 butadeine (106-99-0)
Carbon tetrafluoride (75-73-0)
Carbon monoxide (630-08-0)
Carbonyl fluoride (353-50-4)
Carbonyl sulfide (463-58-1)
Chlorine (7782-50-5)
Chlorine dioxide (10049-04-4)
Chlorine trifluoride (7790-91-2)
Cyanogens (460-19-5)
Cyanogen chloride (506-77-4)
Diborane (19278-45-7)
Dichlorosilane (4109-96-0)
Dimethylamine (124-40-3)
Fluorine (7782-41-4)
Germane (7782-65-2)
Hydrogen bromide (10035-10-6)
Hydrogen chloride (7647-01-0)
Hydrogen cyanide (74-90-8)
Hydrogen fluoride (7664-39-3)
Hydrogen selenide (7783-07-5)
Hydrogen sulfide (7783-06-4)
Methyl bromide (74-83-9)
Methyl fluoride (593-53-3)
Methylisocyanate (624-83-9)
Nickel carbonyl (13463-39-3)
Nitric oxide (10102-43-9)
Nitrogen dioxide (10102-44-0)
Nitrogen trifluoride (7783-54-2)
Phosgene (75-44-5)
Phosphine (7803-51-2)
Phosphorus oxychloride (10025-87-3) Phosphorus pentafluoride (7647-19-0)
Phosphorus trichloride (7719-12-2)
Phosphorus trifluoride (7783-55-3)
Selenium Hexafluoride (7783-79-1) Silane (7803-62-5)
Silicon tetrachloride (10026-04-7)
Silicon tetrafluoride (7783-61-1)

Stibine (7803-52-3)
Sulfuryl fluoride (2699-79-8)
Tellurium hexafluoride (7783-80-4)
Titanium tetrachloride (7550-45-0)
Trichlorosilane (10025-78-2)
Trimethyl aluminum (75-24-1)
Trimethyl boron (593-90-8)
Trimethyl gallium (1445-79-0)
Tungsten hexafluoride (7783-82-6)
Vinyl chloride (75-01-4)