<u>The Dangerous Gas Program</u>

Scope

The main purpose of the Dangerous Gas Program is to provide guidelines that will promote safe and healthy environment for researchers, building occupants or emergency responders (exposure or gas leak events) by establishing minimum standards and safe practices that will reduce the likelihood of accidental release of a dangerous gas.

Gases classified as toxic, highly toxic, corrosive, flammable and pyrophoric with any of the following characteristics will fall under the Dangerous Gas Program:

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

Below are definitions for pyrophoric, flammable, corrosive, toxic and highly toxic gases.

Pyrophoric: Gas that will ignite spontaneously upon contact with air at or below a temperature of 54.4 degrees Celsius (130 degree Fahrenheit)

Toxic: Gas with a Lethal Concentration (LC) 50 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 200 ppm or less 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.

Corrosive: Acidic or basic gases that will attack and damage human tissue. They will also link damage metals and other building materials.

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

I. Is ignitable at 14.7 psia (101 kPa) when in a mixture of 13 percent or less by volume with air; or

II. 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.

Dangerous Gas Pre-Purchase Notification

Dangerous gas purchase requires pre-purchase notification to Risk Management and Safety (RMS). Toxic and dangerously reactive gases should only be purchased from vendors who will agree to take back empty gas cylinders.

The Dangerous Gas Pre-Purchase Notification Form will provide preliminary information to RMS who will determine if appropriate safety control measures are in place prior to the acquisition of dangerous gases.

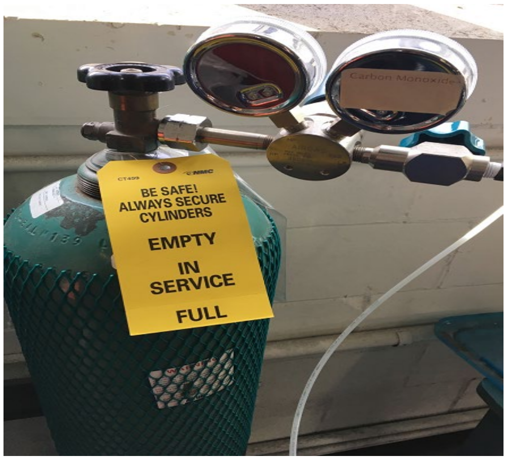
Pre-Purchase Process

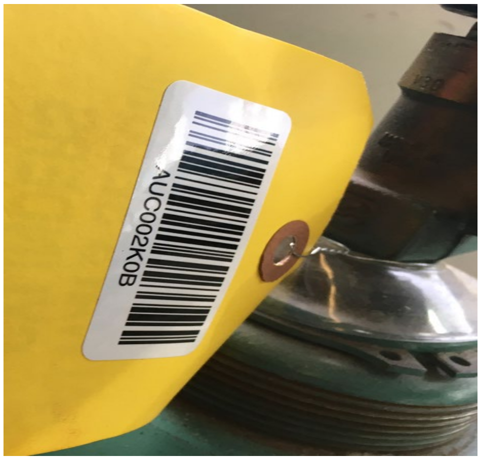
1. Complete the Dangerous Gas Pre-Purchase Notification Form prior to each purchase and submit form to RMS.
2. RMS will review the information provided on the form then contact you to approve the purchase or
3. RMS will review the information provided on the form and work with you to ensure that proper safety control measures are in place before dangerous gas purchase is completed.

Management of Dangerous Gases

I. Inventory

Cylinders containing dangerous gases should be inventoried upon receipt. Hanging tags with barcodes will be utilized to simplify verification through our online hazardous chemicals management system (Chematix). The hangtag should be attached to the cylinder. The same hangtag can be used if replacing similar gas and quantities.





II. Storage, Handling and Use Requirements

General guidelines

Read all label information and Safety Data Sheets (SDS) before using dangerous gases. Only qualified / trained personnel should perform dangerous gas cylinders change out. These change out procedures should be documented.

Never tamper with pressure relief devices in valves or cylinders. Lecture bottles don't have pressure relief devices; they have identical valve threads regardless of the contents. Contact RMS or the supplier if labels and valve tags do not agree or contents of a lecture bottle are questionable. It is recommended to purchase returnable gas cylinders.

Dangerous gas cylinders should be stored in continuously ventilated gas cabinets that are equipped with excess flow control devices and fire suppression systems. Lecture bottles should be in gas cabinets or inside fume hoods during storage and use.

Mark designated areas (with proper warnings) within a lab where toxic or dangerous gases are used. If feasible, purchase less concentrated gas cylinders below known dangerous levels to minimize exposure risks.

Use of dangerous gases in processes that pose a risk of explosion or are highly exothermic should be conducted in a fume hood with the sash in its lowest feasible position.

In the event of power failure, exhaust ventilation, gas monitoring and emergency notification systems should continue to operate or dangerous gas systems should automatically shutdown at the source.

Ventilation and hardware requirements

Proper ventilation is required in areas where dangerous compressed gas cylinders are used. Reaction vessels and chambers should be in fume hoods. RMS will assess the need for additional controls if research equipment cannot be located inside the fume hood.

RMS will evaluate whether appropriate ventilation systems are in place before dangerous gases are purchased. Fume hoods, ventilated gas cabinets or other specialty local ventilation exhaust systems / enclosures are required in labs where dangerous gases are stored and manipulated. Ventilation monitors should be installed on chemical fume hoods or gas cabinets where dangerous gases are used to measure duct or enclosure exhaust performance. Lab personnel are required to be trained on monitor functions and what to do if ventilation fails. Ventilation monitoring interlocked with automatic gas shutdown may be required for highly toxic gases, or for unattended operations using highly toxic and extremely reactive gases.

Ventilated gas cabinets housing dangerous gases should meet the following requirements:

- Must be connected to an exhaust system and be equipped with automatic shut off valves and excess flow devices
- Operate at negative pressure in relation to surrounding environment. Gas cabinets should have an average face velocity of ~200 fpm with a minimum of ~ 150 fpm at any part of the access port or window.
- Should have self-closing doors constructed of at least 0.097 inch (12 gauge) steel
- Must be internally sprinklered and should not have more than 3 dangerous gas cylinders.

Process specific operating procedures should include safety apparatus features present, e.g. restricted flow orifice (RFO), excess flow valves, emergency shutoff valves etc. All dangerous gas cylinders should have a restricted flow orifice installed to limit the maximum gas release rate in the event of an accidental release. If feasible, flow restricting devices must be installed after the regulator. Leak check procedures for piping systems should be included in process safety procedures.

Full sized gas cylinders should be dispensed using a two-stage regulator. Two stage regulator devices control pressure in two steps by reducing high pressure in the gas cylinder to a lower working pressure. The maximum pressure of the second stage of the regulator should be as low as is practical for the intended experimental work.

Dangerous gases must be dispensed through tubing and piping systems that have been properly cleaned and are compatible with the gas in use. All tubing used for dangerous gases will be stainless steel unless contraindicated due to chemical incompatibility. Tubing should be free of scratches, possess no uneven seams and be suitable for bending and flaring without kinking at the bend radius used. Tubing used for toxic and pyrophoric gases should not be made of combustible materials. Always use stainless steel tubing for delivering gases into high temperature processes e.g., in ovens or furnaces.

Five valve purge panels with venturi e.g., Matheson PAN- 5500 or equivalent are recommended when purging toxic or pyrophoric gases. Exhausted dangerous gas emissions from mechanical exhaust systems (lines, ducts etc.) should present no potential for re-entrainment into any building supply air intake or occupied areas. Significant emissions of corrosive or toxic gases require an emission control device (e.g., scrubber, flare device, adsorbent) before the purged gas can be vented into the exhaust duct system. Significant emissions are defined as duct concentrations that could result in duct corrosion or acute health risk to persons exposed near exhaust fan stacks.

Gas Detection Systems, Alarm Monitoring and Emergency Response Notification Requirements

RMS will review gas monitoring equipment with the Principal Investigator (PI) before it is purchased. This is to evaluate suitable gas monitoring systems, define alarm set points, specify calibration requirements, and have uniform alarm notifications and response. RMS may add gas monitoring devices in BioRAFT for inventory and calibration reminders. A continuous monitoring system is that which is permanently installed and is required to be online during gas use. Detection by the monitor at any sampling point should be within 30 seconds at the Permissible Exposure Limit (PEL) concentration or as defined by the PI and RMS. Temporary monitoring systems are portable and are utilized by lab personnel when operating dangerous gas cylinders, experiments must be continuously attended when using these monitors.

Continuous gas monitoring is required when using dangerous gases at Auburn University with an exception of the following:

(i) Gas cylinders whose concentration (ppm) is less than the National Institute for Occupational Safety and Health (NIOSH) Immediately Dangerous to Life and Health (IDLH) levels. RMS and the PI will evaluate the need for continuous monitoring if an IDLH concentration is not available and the gas cylinder concentration is greater than the PEL. Temporary monitoring system is to be utilized during gas use, experiments must be continuously attended while the gas cylinder is open and provisions for remote shutoff should be provided.

(ii) Lecture bottles whose use is restricted inside of fume hoods i.e. not “plumbed” to processes outside of the fume hood. Temporary monitoring system is to be utilized during gas use, experiments must be continuously attended while the gas cylinder is open and provisions for remote shutoff should be provided. If their use is not limited to inside the hood, i.e., “plumbed” to equipment outside the hood, they must be equipped with excess flow control devices and continuous monitoring must be done at the point where the gas line enters the tool, and in the area where the operator is located

(iii) Pyrophoric gases are to be monitored continuously except when the concentration is below the pyrophoric limit. The process in which they are being used should not concentrate the pyrophoric material. Another exception will be for lecture bottles with restricting orifice in the CGA cylinder valve that are exhausted or used in a vacuum system that can fully evacuate the cylinder. The vacuum exhaust should be purged with Nitrogen.

Sensing ports should be located in the gas cabinets, at the point of operation and in the general lab operator area. Sensors should provide alarm communication that is visual and audible for example, a buzzer or flashing strobe so the laboratory occupant(s) can take corrective action. Alarm set off points should be at the PEL levels or lower. Main readout panels should be located immediately outside the lab for personnel to read as they exit the lab.

Gas monitoring systems should be designed to interface with the building fire alarm notification systems. PIs should have alarm notification and response procedures documented. Contact names and numbers must be provided for on and off hour response.

The PI is responsible for procurement of gas monitoring systems. RMS will review with PI prior to purchase. They are also responsible for training lab personnel on gas monitoring procedures which includes operation of the monitor, calibration (according to manufacturer's recommendations) and emergency response plan. This should be done before dangerous gas is used.

Building alarm conditions are automatically communicated to Auburn University Campus Safety. Alarm readouts should be in a location (immediately outside a lab) such that the emergency response personnel can read alarm conditions without entering a danger zone. Information such as alarm location, set points, type of gas being monitored and real time concentrations will be useful for emergency response personnel.

When local alarms go off; the emergency shut off systems should be activated. Gas shutoff can be achieved via high pressure pneumatically controlled emergency shut off valves in the gas cabinets, air actuated cylinder valves or gas control box of equipment in use if feasible. Visual and audible alarms should be activated followed by emergency response plan.

Job Hazard Analysis and Integration of Safety in Lab Procedures

RMS together with PIs will conduct hazard evaluation to identify, evaluate and control hazards before dangerous gases are used. This will involve evaluation of health risks posed by dangerous gases, process safety, and gas monitoring needs. Lab personnel should be properly trained on emergency response and notification procedures in the event of accidental release. Here is a summary of safety checks that should be done before dangerous gases are used in research:

- Review and documentation of intrinsic properties of dangerous gases and other chemicals used in lab procedures, dangerous gas cylinder change out procedures should also be included.
- Review and documentation of physical hazards associated with the process, equipment in use and possible consequences in the event of catastrophic failure of safety controls in place.
- Review of engineering controls, administrative controls and personal protective equipment used for hazard mitigation.
- Process specific training and documentation for lab personnel using dangerous gases. Training should include emergency response procedures, operation, maintenance and/ or calibration of gas sensing or monitoring systems according to manufacturer's recommendations.
- Documentation and review of incident / near-miss follow up procedures including lessons learned.

References

(i) University of North Carolina, EH&S, Laboratory Design Guidelines

(ii) University of Pennsylvania, Environmental Health and Radiation Safety, Hazardous and Highly Toxic Gases

(iii) Georgia Tech Dangerous Gas Safety Program

(iv) Clemson University, Dangerous Gas Standard

(v) Stanford University, Toxic Gas Standard Operating Procedures

(vi) North Carolina State, EH&S, Gas Monitoring Program

(vii) International Fire Code, IFC 2012 Edition

(viii) NFPA 1, Chapter 3, 2012 Edition

(ix) NFPA 45, Chapter 8

(x) NFPA 55, Chapter 3

(xi) NFPA 704, Chapter 5

(xii) ANSI/CGA-G-13 – 2015 Edition -- (American National Standards Institute / Compressed Gas Association) – Storage and Handling of Silane and Silane Mixtures

Examples of Common Dangerous Gases

Below is a list of toxic gases that must be stored under continuous ventilation either in a fume hood or ventilated gas cabinet. Purchasing these gases requires Risk Management and Safety (RMS) pre-approval. RMS will verify proper storage, inventory, and hazard mitigation plans.

Gas	CAS	Hazards	Threshold Levels	NFPA Ranking
Ammonia	7664-41-7	Corrosive	TLV:25 ppm PEL:50 ppm IDHL:300 ppm	3
Arsine	7784-42-1	Highly toxic, flammable, pyrophoric	TLV:0.05 ppm PEL:0.05 ppm IDHL:3 ppm	4
Boron Tribromide	10294-33-4	Toxic, corrosive	TLV:1 ppm PEL:1 ppm IDHL:50 ppm	3
Boron Trichloride	10294-34-5	Toxic, corrosive	TLV:5 ppm PEL:5 ppm IDHL:25 ppm	3
Boron Trifluoride	7637-07-2	Toxic, corrosive	TLV:1 ppm PEL:1 ppm IDHL:25 ppm	3
Bromine	7726-95-6	Highly toxic, corrosive, oxidizer	TLV:0.1 ppm PEL:0.1 ppm IDHL:3 ppm	3
Carbon Dioxide	124-38-9	Simple asphyxiant	TLV:5000 ppm	

			PEL:5000 ppm IDHL:40000 ppm	
Carbon Monoxide	630-08-0	Toxic, Flammable	TLV:25 ppm PEL:25 ppm IDHL:1200 ppm	3
Chlorine	7782-50-5	Toxic, corrosive, oxidizer	TLV:0.5ppm PEL:1 ppm IDHL:10 ppm	3
Chlorine Dioxide	10049-04-4	Toxic, Corrosive, Oxidizer	TLV:0.1 ppm PEL:0.1 ppm IDHL:5 ppm	
Chlorine Trifluoride	7790-91-2	Toxic, corrosive, oxidizer	TLV:0.1 ppm PEL:0.1 ppm IDHL:12 ppm	4
Diborane	19278-45-7	Highly toxic, flammable, pyrophoric	TLV:0.1 ppm PEL:0.1 ppm IDHL:15 ppm	4
Dichlorosilane	4109-96-0	Toxic, corrosive, flammable	TLV:2 ppm PEL:5 ppm IDHL:50 ppm	4
Dimethylamine	124-40-3		TLV:5 ppm PEL:10 ppm IDHL:500 ppm	3
Ethylene Oxide	75-21-8	Toxic, flammable	TLV:1 ppm PEL:1 ppm IDHL:800 ppm	3
Fluorine	7782-41-4	Highly toxic, corrosive, oxidizer	TLV:0.1 ppm PEL:0.1 ppm	4

			IDHL:25 ppm	
Germane	7782-65-2	Highly toxic, flammable, pyrophoric	TLV:0.2 ppm PEL:0.2 ppm IDHL:6 ppm	4
Hydrogen Bromide	10035-10-6	Toxic, corrosive,	TLV:3 ppm PEL:3 ppm IDHL:30 ppm	3
Hydrogen Chloride	7647-01-0	Toxic, corrosive,	TLV:5 ppm PEL:5 ppm IDHL:50 ppm	3
Hydrogen Fluoride	7664-39-3	Toxic, corrosive,	TLV:0.5 ppm PEL:3 ppm IDHL:30 ppm	4
Hydrogen Cyanide	74-90-8	Highly toxic, flammable	TLV:10 ppm PEL:10 ppm IDHL:50 ppm	4
Hydrogen Selenide	7783-07-5	Highly toxic, flammable	TLV:0.05 ppm PEL:0.05 ppm IDHL:1 ppm	4
Hydrogen Sulfide	7783-06-4	Toxic, flammable, corrosive	TLV:10 ppm PEL:10 ppm IDHL:100 ppm	4
Methyl Bromide	74-83-9	Toxic, flammable	TLV:1 ppm PEL:1 ppm IDHL:250 ppm	3
Methyl Isocyanate	624-83-9	Highly toxic, flammable	TLV: 0.02 ppm PEL:0.02 ppm IDHL:3 ppm	4

Methyl Mercaptan	74-93-1	Toxic, flammable	TLV:0.5 ppm PEL:0.5 ppm IDHL:150 ppm	4
Methylamine	74-89-5	Flammable, corrosive	TLV:5 ppm PEL:10 ppm IDHL:100 ppm	3
Nickel Carbonyl	13463-39-3	Highly toxic, flammable	TLV: 0.05ppm PEL:0.001 ppm IDHL:2 ppm	4
Nitric Oxide	10102-43-9	Highly toxic, oxidizer, corrosive	TLV:25 ppm PEL:25 ppm IDHL:100 ppm	3
Nitrogen Dioxide	10102-44-0	Highly toxic, oxidizer, corrosive	TLV:3 ppm PEL:5 ppm IDHL:20 ppm	3
Ozone	10028-15-6	Highly toxic, oxidizer	TLV:0.05 ppm PEL:0.1 ppm IDHL:3 ppm	
Phosgene	75-44-5	Highly toxic	TLV:0.1 ppm PEL:0.1 ppm IDHL:2 ppm	4
Phosphine	7803-51-2	Highly toxic, flammable, pyrophoric	TLV:0.3 ppm PEL:0.3 ppm IDHL:50 ppm	4
Phosphorus Oxychloride	10025-87-3	Highly toxic	TLV:0.1 ppm PEL:0.5 ppm IDHL:1 ppm	4

Phosphorus Pentafluoride	7647-19-0	Toxic, corrosive	TLV:0.1 ppm PEL:1 ppm IDHL:50 ppm	
Phosphorous Trichloride	7719-12-2	Toxic, corrosive	TLV:0.2 ppm PEL: 0.5 ppm IDHL: 25 ppm	4
Selenium Hexafluoride	7783-79-1	Highly toxic	TLV:0.05 ppm PEL: 0.05 ppm IDHL:2 ppm	
Silane	7803-62-5	Pyrophoric	TLV:5 ppm PEL:5 ppm	4
Silicon Tetrafluoride	7783-61-1	Toxic, corrosive		3
Stibine	7803-52-3	Highly toxic, flammable,	TLV:0.1 ppm PEL:0.1 ppm IDHL:5 ppm	4
Sulfur Dioxide	7446-09-5	Toxic, corrosive	TLV:2 ppm PEL:2 ppm IDHL:100 ppm	3
Sulfuryl Fluoride	2699-79-8	Corrosive	TLV: 5 ppm PEL: 5 ppm IDHL:200 ppm	4
Tellurium Hexafluoride	7783-80-4	Highly Toxic	TLV: 0.02 ppm PEL: 0.02 ppm IDHL:1 ppm	
Tetrafluoroethylene	116-14-3	Flammable, peroxidizable	TLV: 2 ppm	4
Triethylamine	121-44-8	Highly flammable, toxic	TLV:2 ppm PEL:2 ppm IDHL:100 ppm	4
Tungsten Hexafluoride	7783-82-6	Toxic, corrosive		4