UC Irvine Environmental Health & Safety

Toxic Gas Program

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UCI Toxic Gas Program

I. Program Objectives

Various toxic, pyrophoric, and other hazardous compressed gases are used on the UC Irvine campus. Due to the potential health, fire and reactivity hazards presented by an accidental release of these gases, Environmental Health & Safety (EH&S) has developed this UCI Toxic Gas Program[1] that outlines the responsibilities of principal investigators and lab managers, students and staff whom they supervise and the EH&S office. The objectives of the Toxic Gas Program cover five important dimensions necessary for the safe practice of toxic gases on campus:

1. Specify safe and established procedures for the transportation, handling, storage, use, and disposal of toxic gases.
2. Establish engineering and administrative controls that reduce the likelihood of an incident involving toxic and highly toxic gases.
3. Provide UCI faculty, staff, and students with resources and strategies for understanding the hazards and controls related to toxic/highly toxic gases and to outline responsibilities of all parties.
4. Ensure that UCI complies with regulatory requirements for toxic gases as dictated by the California Fire Code (CFC) & California Occupational Safety and Health Administration (Cal/OSHA) etc.
5. Outline emergency response procedures for toxic gas releases for all parties including emergency responders.

II. Scope & Applicability

Scope

This program covers all labs, facilities and storage sites on campus that handle or use toxic, highly toxic or pyrophoric gases. All gases in this program ADDITIONALLY need to comply with the UCI Compressed Gas Program. Guidelines will depend on factors such as inventory amounts, concentration levels (referencing both the IDLH, *Immediately Dangerous to Life and Health* and PEL, *Permissible Exposure Limits* concentrations) and inherent danger of the gas (toxicity and other hazards). Toxic gases listed in Table 1 are currently being used on campus; this program will also cover all new toxic gases introduced to the campus (See Appendix Table A2 for a full list).

Table 1 –Toxic Gases Used at UCI		
Anhydrous Ammonia	Fluorine	Nitrous Oxide
Boron Trichloride	Hydrogen Bromide	Nitrogen Dioxide
Boron Trifluoride	Hydrogen Chloride	Phosphine
Carbon Monoxide	Hydrogen Sulfide	Silane
Chlorine	Methyl Bromide	Silicon Tetrafluoride
Diborane	Methyl Mercaptan	Sulfur Dioxide
Dichlorosilane	Nitric Oxide	Xenon Difluoride

All parties involved in toxic gas use should read this program in its entirety as every section covers an important aspect of compliance.

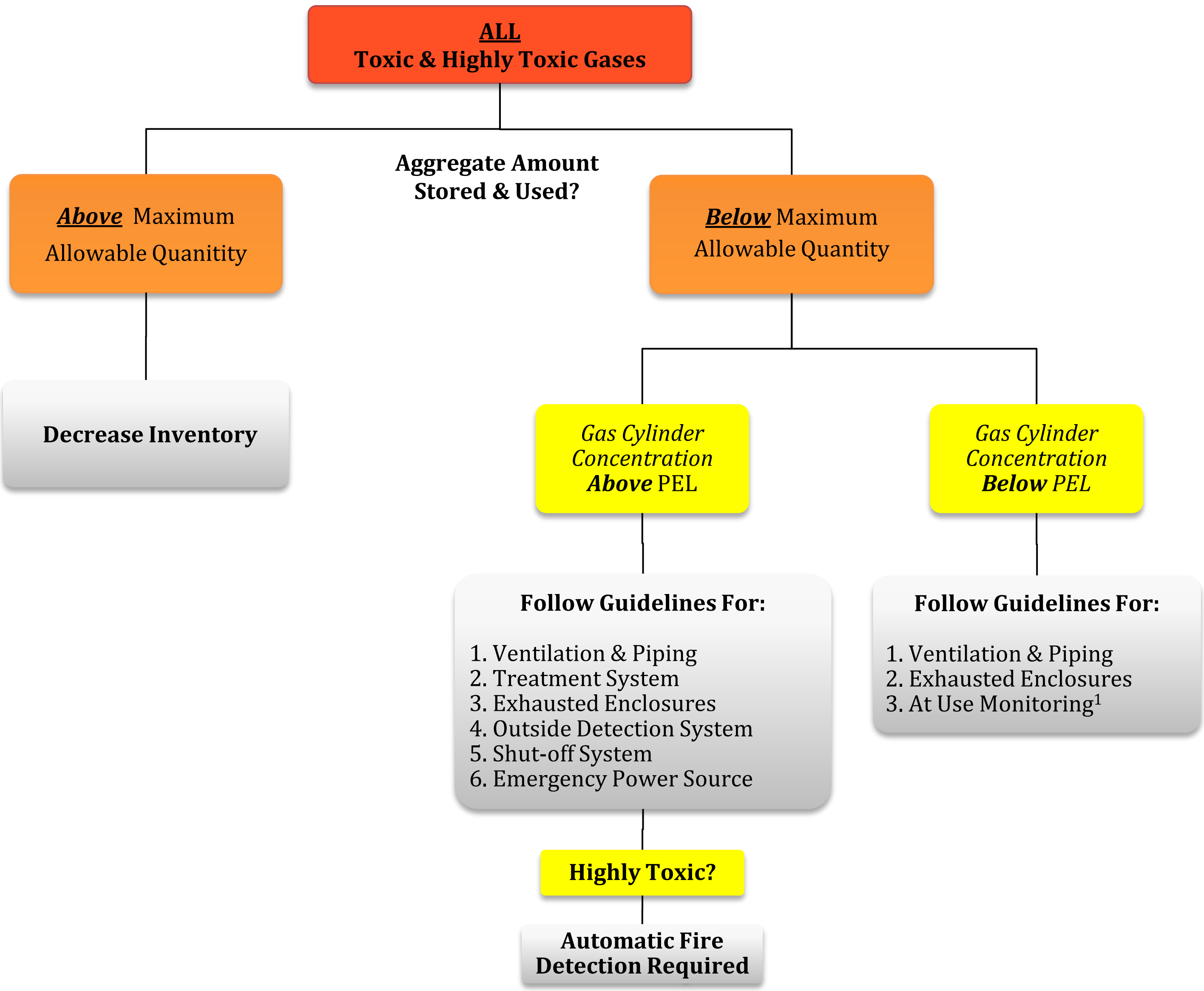
Applicability

Because various levels of rigor exist for different toxic and highly toxic gas usage, this program has outlined a few rules for determining which guidelines your lab should follow:

- **Administrative Controls:** To be followed by ALL toxic and highly toxic gas users regardless of inventory amounts.
- **Engineering Controls**: Determine applicability using the flow chart in Figure 1; all engineering controls are mandatory by law. Table 2 and A2 (Appendix) define inventory amounts and concentrations to which the flowchart refers, respectively. See chapter 5 for details on engineering controls.

[1]*This version of the program is based on the 2013 CFC, as it is published every 3 years, users should be aware of potential amendments to the CFC and corresponding changes to guidelines.*

Figure 1-Flow Chart for Determining Toxic Gas Compliance Guidelines



Notes:

- Due to multiple factors limiting maximum allowable quantities (such as building occupancy and floor level), EH&S will perform an individualized assessment for every lab to determine allowed quantities.
- Maximum Allowable Quantities must be calculated independently for toxic and highly toxic gases. Labs must not supersede the maximum allowable quantity for either category.
- All inventories must be in approved exhausted enclosures.
- Guidelines for each control are explained in Chapter 5 of this program.

[1]At use monitoring: Monitoring that is only required when the main cylinder valve is open even when no active experiments are running and no personnel are present. If gas lines are connected to a process, monitoring must occur at all points of connections.

III. Special Scope: Toxic Gases as By-Products

The scope of this program incorporates toxic gas releases also as secondary hazards-i.e. as unintended or accidental by-products resulting from other reactions or accidents. For these cases, controls will be discussed only in the capacity of emergency guidelines and hazard control measures. In other words, procedures will be outlined should an unintended reaction result in a toxic gas release.

There are two very common ways in which toxic gas by-products can be produced. The first is a simple interaction with water by some solid compounds. Such water reactive chemicals should be treated with caution. The second manner is through incompatible chemical reactions. Table 2 summarizes common reactive incompatibilities and the toxic gases they produce:

Table 2-Reactions Causing Toxic Gas Releases

Any: +	Any: →	Toxic Gas Produced
Arsenic compounds	Any reducing agent	**Arsine**
Azides	Acidic compounds	**Hydrogen azide**
Cyanides	Acidic compounds	**Hydrogen cyanide**
Hypochlorites	Acidic compounds	**Chlorine or Hypochlorous acid**
Nitrates	Sulfuric acid	**Nitrogen dioxide**
Nitric acid	Copper, brass, any heavy metals	**Nitrogen dioxide (nitrous fumes)**
Nitrites	Acidic compounds	**Nitrous fumes**
Phosphorus	Caustic alkalis or reducing agents	**Phosphine**
Selenides	Reducing agents	**Hydrogen selenide**
Sulfides	Acidic compounds	**Hydrogen sulfide**
Tellurides	Reducing agents	**Hydrogen telluride**

Research personnel should be familiar with this list and water reactive compounds, keeping a copy handy in all labs with chemical solids. If a released gas from a reaction is identified to be toxic, the same emergency response and evacuation procedures should be followed as outlined in this program AND relevant Safety Data Sheets should be consulted.

IV. Purchasing & Acquisition

All toxic and highly toxic gas purchases must be requisitioned through the UCI Purchasing Department as a high value requisition and require approval from EH&S. EH&S will approve the purchase after ensuring that proper controls are present and that engineering controls are in place prior to arrival of the toxic gas. Training tools and documents such as Standard Operating Procedures and basic lab training will also be reviewed prior to approval.

V. Responsibilities

The following outlines the responsibilities of all parties including the principal investigator, lab personnel and Environmental Health and Safety.

Responsibilities: **Principal Investigators & Lab Managers**	*The principal investigator carries the primary responsibility of ensuring that there is no potential of harm/exposure from toxic gases and that all safety roles and responsibilities are being performed appropriately and per regulations. Tasks can be delegated to trained personnel, however it is the ulimate responsibility of the PI to ensure the following:*
	1. All lab personnel using toxic gases have **documented** training on the following: a. *Lab Safety Fundamentals (www.uclc.edu)* b. *Compressed Gas Training*-hands-on training showing different types of regulators, changing regulators, performing leak tests, etc. (Sign on using www.uclc.edu) c. *Toxic Gas Program*-including engineering controls (this document) d. *Safety Data Sheets* for all toxic gases in the lab e. Written *Standard Operating Procedures* (SOPs) using toxic gases
	2. All aspects of the Toxic Gas Program are followed, engineering controls are being mantained, and appropriate PPE is provided and used by lab personnel.
	3. A minimum of two people are in the lab when toxic gases are being used.
	4. Up-to-date Safety Data Sheets, Emergency Response and Evacuation Procedures are available and **reviewed by both users and non-users of toxic gases.**
	5. The lab's chemical inventory list with the names and quantities of toxic gases is updated and EH&S is notified regarding any changes in toxic gas uses (also works with EH&S to develop a Risk Management & Prevention Program (RMPP) if required by the changes).
	6. Toxic gas monitors are approved by EH&S, properly maintained and gas sensors are calibrated (with documentation) and replaced at a frequency per manufacturer's recommendations. Ventilation airflow labels on gas cabinets and fume hoods are tested within the past 12 months and EH&S is notified if past due.
	7. Toxic gas **purchasing specifications** (i.e., volumes, concentrations etc.) are specificed for both new and renewed toxic gas purchases with Purchasing Department and EH&S.
	8. Information from the vendor regarding gas volume at Standard Temperature and Pressure (STP), chemical compatibility with process equipment and materials, manifold specifications, and availability of Restrictive Flow Orfice (RFO) is obtained prior to ordering.
	9. The gas vendor is notified when empty/partially full cylinders are ready for pickup.
	10. Lab safety inspections of toxic gases are conducted before new procedures and at least monthly otherwise and deficiencies are corrected within a reasonable time period.
	*All **On-site** responsibilties apply to lab managers if the facility is shared. Training, SOPs and other administrative controls are always the responsibility of the PI non-users' training.

Responsibilities:

Environmental Health & Safety

UC Irvine Environmental Health and Safety bears the responsibility of overseeing compliance for the toxic gas program, making sure the labs and facilities are in full compliance with state and local regulations. EH&S also guides the principal investigator / researchers on safe practices and issues presented.

Reviews and approves all requests for new toxic gas purchases and uses based on potential hazards and available hazard controls, in cooperation with the PI and Purchasing Department.

Assists Principal Investigator in developing safety procedures and selecting appropriate equipment for the proposed use of toxic gases based on the degree of hazard.

Contacts the PI/gas user/requestor to get additional information, if needed, to perform a detailed hazard assessment and safety evaluation of a proposed new toxic gas use in order to determine what safety controls will be required.

Notifies the department and PI if the gas type and requested amount may require a Risk Management and Prevention Program (RMPP), and if so, assists the PI in developing an RMPP.

Acts as the primary campus contact for regulatory agency inspections, performs an ***annual regulatory compliance inspection*** of the written UCI Toxic Gas Program and updates it if necessary.

Recommends gas monitors for certain toxic gas applications or processes, checks the calibration records and/or verifies that gas monitors are working properly during periodic inspections.

Works with the PI and the Campus Fire Marshal to review and possibly approve a proposed toxic gas purchase that may require a change in the laboratory's Occupancy (moving labs to a higher occupany building), based upon the California Building and Fire Code requirements.

Notifies the PI if the gas use plans are not approved with the current lab setup, assists the department in addressing deficiencies and in implementing safety modifications to help the lab meet the requirements for approval.

Maintains EH&S inventory list of the ventilated gas cabinets and fume hoods that are tracked by serial numbers.

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Responsibilities:

Toxic Gas Users

Researchers, being the primary users of toxic gases need to be cautious, cooperative and inquisitive regarding the use of toxic gases. The following repsonsibilities required of all researchers:

Perform a Safety Training Self Assessment (STSA) both online and with their PI and completes all required training including:

1. *Lab Safety Fundamentals (Sign on using www.uclc.uci.edu)*
2. *Compressed Gas Training (Sign on using www.uclc.uci.edu)*
3. *Toxic Gas Program*-specific hands on training with the PI must be included
4. *Safety Data Sheets* for all toxic gases in the lab
5. Any written *Standard Operating Procedures* (SOPs) using toxic gases

May participate in the writing of process SOPs and performs a hazard analysis of the process along with the principal investigator. Informs EH&S of new toxic gas uses AND lab peers of toxic gas usage outside of exhausted enclosures (ex. gas line connected to instrument, process equipment).

Are required to label all areas, gas lines and equipment in the lab involving toxic gases. Designated areas must also be planned and communicated to all lab members.

Learn all assigned responsibilities from the PI including monitors, alarms, sensors and other safety engineering controls.

Understand all regulations, PPE and controls outlined in the UCI Toxic Gas Program.

Understand and is innately familiar with Emergency Shut-off and evacuation procedures.

Understand and is innately familiar with emergency plan pertaining to toxic gases including actions following accidental release and/or physical contact.

Responsibilities:

Non-Users in labs with Toxic Gases

Personnel not using or handling a toxic gas must attain a level of knowledge to safely respond to a toxic gas emergency. The PI carries the responsibility of informing non-users of the prescence of toxic gases and their responsibilities as follows:

Completion of all assigned training including SDSs and hands-on training with the Principal Investigator regarding responses to toxic gas emergencies.

Understanding and innate familiarity with Emergency Evacuation Procedures as written in the lab's Emergency response plan. **Non-users must participate in emegergency drills for toxic gas emergencies.**

Understanding and innate familiarity with the emergency plan pertaining to toxic gases including action following accidental releases and/or physiological exposure.

VI. Program Components

This section explains the implementation of responsibilities outlined in the previous section. When reviewing responsibilities, researchers and principal investigators should refer to these sections for clarification. This program will establish three main components for the safe use of toxic gases on both preventive and mitigative levels. Each party must understand when and how to apply each safety control. The following is a simplified outline of the program components:

a. Personal Protective Equipment- PPE
b. Administrative Controls (Safe Handling, Behavioral Practices & Guidelines etc.)
c. Engineering Controls (Monitors, Alarms, Shut-Off Valves, etc.)

Work Alone is never permitted during operations involving toxic gases. At least one other person must be present in the same room when work involving toxic gases is performed.

5.1 Personal Protective Equipment

NOTE:
All PPE MUST be inspected for wear, damage or contamination prior to use. Always consider potential interaction with other chemicals/agents in the same experiment during PPE selection.

ALWAYS REQUIRED	**Eye Protection**: Safety glasses with side shields, or tightly fitting safety goggles, should be worn whenever working with gases in the laboratory.
	Skin Protection: Long pants and shirts (cotton-based, non-synthetic, lab coats (possibly flame-resistant if fire hazard exists), and closed-toe and closed-heel shoes must be worn whenever working with toxic gases. The lab coat sleeves must fully extend to the wrists and the front must be completely buttoned at all times.
Sometimes REQUIRED	**Hand Protection**: Leather or cut-resistant gloves should be used when handling gas cylinders to protect against cuts and pinch point hazards. Rubber, chemical-resistant gloves are needed if contact with the gas or its liquefied state is anticipated (ex. connecting the regulator/pressure gauge assembly). Selection of the correct glove depends on the specific gas and the anticipated degree of contact, therefore the SDS should be reviewed to determine glove compatibility.
	Steel-toed safety shoes are recommended for handling and moving compressed gas cylinders to protect the toes against cylinder rolling hazards.
	Faceshields worn over the safety glasses/goggles may be required for certain tasks or processes.
	Respiratory protection is usually not required for normal, day-to-day gas use. See SDS for each gas for requirements. Respirators should be available in case of a release.
	Supplemental equipment, such as **blast shields**, should be used when working with toxic gases or processes that may result in explosions or pressure releases.

5.2 Administrative Controls

Administrative controls are pre-operational safety practices that reduce or eliminate the risk and impact of hazards. Following administrative controls relies heavily on instilling a strong culture of safety within the research group.

Administrative Controls:
Transportation Policies

Vendor Transportation: All toxic gas vendors or suppliers must comply with DOT regulations regarding the transportation of toxic gases while on campus property.

Delivery: The gas vendor will deliver the cylinder directly to the lab where the gas will be used.

On campus transportation of toxic gases by UCI personnel must only be done using university vehicles- personal vehicles are never permitted even for small lecture bottles.
No off-campus transportation is allowed. The following rules must be adhered to:

-The cylinder valve safety cap **must remain in place to protect the valve.**
-Gas cylinders must be properly secured to the transport vehicle at all times to prevent any movement using a 2-point restraint system with upper & lower restraints on the cylinder body.
-An open truck with a separate cab should be used. If an enclosed truck is used, the gas cylinders should be leak tested before transporting.
-The transport vehicle must be continuously occupied by the driver, even when parked.
-The cylinder should not be rolled, dragged, slid across the floor, or lifted by the cylinder cap or valve assembly. The gas cylinder should not be left unattended while being transported indoors.
-Appropriate elevator transport guidelines must be followed.

Upon Lab Receival

Upon entering the lab/facility the cylinder should be placed in an exhausted enclosure. Either the vendor representative or a trained university employee should connect the regulator and pressure gauge assembly to the cylinder CGA valve. The cylinder valve safety cap should be left in place at all times when the gas cylinder is not in use.

All toxic gas cylinders must be stored in a **vertical, upright position double-chained (one-third from the top and one-third from the bottom on the building infrastructure**) with the valve end up. **C-clamps or bench mounting brackets are prohibited unless specified by the manufacturer as OSHA-compliant and should only be used on a temporary basis.**

Inventory should be updated immediately.

The cylinder should be checked for clear labeling with the identity of the gas and appropriate hazard warnings (i.e., DOT colored-coded diamond labels).

The gas cylinder connection should be leak tested with a leak indicating solution immediatley after attachment to the system. If the gas flow does not immediately start when the valve is opened slightly, the tester should check for a plug in the valve.

The cylinder gas cabinets **AND gas lines** must be labeled with the name of the gas. The gas lines **should be marked with arrows** indicating the direction of gas flow. A system of color codes may be used in conjunction with the direction arrows to mark flow.

Documentation

Safety Data Sheets (SDS) for each gas should be reviewed before first use of a gas.
A HARD COPY must be HUNG in the lab near the exit.

Standard Operating Procedures that are process and lab specific describing gas usage must be acessible and preferabely hung if frequently used. SOPs are required to include hazard control measures and emergency shut-down procedures for the specific gas. Applications for which the gas is not compatible should be clearly outlined. **PI Consultation** MUST always take place if there will be a scale-up or if there are revisions to the SOP, however minor the revision may be.

Designated Areas must be identified for high-hazard work operations; either the entire laboratory or a portion of the laboratory.

Administrative Controls: **Storage: Area/Location Requirements**	Gas cylinders and associated piping must be bolted or seismically secured to a substantial, fixed surface made out of non-combustible material.
	Gang chaining of multiple cylinders is NOT allowed. Small lecture bottles must be secured to a stable surface and the **valve must be protected from hindrance and/or damage**.
	Storage area locations must have appropriate warning signs in place (Toxic, Corrosive etc.).
	Outdoor storage is allowed on a short-term basis in a secured, locked area at least 75 feet from an exterior door, window, or ventilation system air intake. Outside storage areas should be covered and cool (to minimize pressure increases that can result from heat or direct sunlight), dry (to deter rust and corrosion), and well ventilated (to dilute gas leaks).
	Indoor storage of all toxic gas cylinders must be in mechanically ventilated and locked exhausted enclosures adhering to the specifications in this program. Never in refrigerated cold or heated rooms.
	Cylinders should not be stored next to doors/corridors or where exits could be obstructed.
	Cylinders in storage or use must be periodically inspected for signs of leaks, deterioration, or corrosion (Twice monthly for stored cylinders and daily for in-use cylinders). Cylinders that appear unsafe or show signs of corrosion, dents, dings, pitting, or bulging must be returned immediately to the gas supplier (by the supplier) and EH&S must be contacted.
	Partially full cylinders that still contain toxic gases must remain in exhausted enclosures or fire code-compliant gas storage rooms until they are picked up by the supplier. Enclosed glove boxes can also be used to isolate and contain the hazards of toxic gases.
Storage: Compatibility Requirements	Compressed gas cylinders should be stored away from incompatible materials-including other compressed gas cylinders. ***NOTE:*** *Lecture bottles use universal threads and valves. Some are interchangeable, increasing the risk of accidentally mixing incompatible materials*.
	Cylinders containing oxidizing gases must be separated from cylinders containing flammable gases by a minimum of 20 feet, OR by a non-combustible wall or partition that is at least five feet high and that has a fire resistance rating of at least 30 minutes.
	Toxic **oxidizing** gases should never be stored near combustible materials.
	Toxic **flammable** gases should never be stored near unprotected electrical connections, ignition or heat sources or fire extinguishers.
	Toxic **corrosive** gases (i.e. ammonia, chlorine, hydrogen chloride/bromide, nitrogen dioxide etc.) must never be stored longer than six months, since cylinders can degrade over time.
	No gas cylinders should be kept longer than five years from the last hydrostatic test date which is usually stamped into the metal just below the neck of the cylinder.

Reduction of Hazardous Material and Waste Collection

Smaller-size cylinders should be purchased when possible to reduce volume and minimize hazardous waste. Gases that will not be completely used should be purchased only from vendors who will accept returns. Therefore, if lecture cylinders are not returnable, the *smallest returnable cylinder* should be purchased if only a small quantity is needed.

- **Full or partially full small** lecture bottles containing hazardous gases are prohibited from regular trash disposal and should be disposed of through the EH&S online system: www.ehs.uci.edu/programs/enviro/.
- **Empty gas cylinders:** Before returned to the supplier, the valve must be closed and the protective valve cap must be screwed back onto the cylinder. They should be labeled "**Empty**" and stored in a designated and marked area (i.e., on or near the building's loading dock) that is physically separated from full cylinders to avoid confusion. Serious back flow can occur when an empty cylinder is attached to a pressurized system.
- **Exhausted fume hoods** should never be used to empty a toxic gas cylinder as a method of disposal.

5.3 Engineering Controls

Engineering controls are supporting devices or features designed to warn, signal, monitor or shut-off accidental releases of toxic gases. These controls will be more sophisticated and automated as the hazard of the toxic gas increases. Engineering controls must be maintained, serviced and calibrated (per manufacturer recommendations) in order to be effective.

Engineering Controls:

Ventilation and Piping

Room Ventilation: Ventilation in rooms with toxic gases must adhere to the following:

-Ventilation rate of at least 1 cfm/square foot of room area,
-Exhaust ventilation must **not be recirculated**,
-Negative pressure ventilation relative to the adjacent occupied spaces (i.e., hallways, offices, classrooms, and other laboratories).

Lines or ducts carrying purged or exhausted emissions of gases must be connected to a mechanical exhaust ventilation system that discharges to a safe location on the roof (i.e. presents no potential for re-entry into building supply air or occupied area). Materials of construction of the exhaust ducts should be chemically resistant to degradation by the gas.

Sprinklers: rooms are required to be sprinklered if they have highly toxic or pyrophoric gases.

Significant emissions of toxic gases may require an emission control device (i.e., wet scrubber, flare device, charcoal adsorbent) before the purged gas can be vented into the exhaust system or to the outdoor environment if corrosion of ducts causes health risks to rooftop workers (near exhaust fan stacks). If exhaust system concentrations pose health risks to workers, then locked gates, doors, or other means shall be used to prevent worker access to stack discharge areas and warning signs must be clearly placed.

Exhausted Enclosures

Exhausted Enclosures are required during both the use and storage of toxic, highly toxic and pyrophoric gases.

Enclosures: All enclosures including toxic gas cabinets, fume hoods[1] or other exhausted enclosures must have an inward airflow velocity (face velocity) at the work opening of **at least 200 fpm** with a **minimum of 150 fpm** at any point of the access port or window.

-A continuously-reading ventilation airflow monitor is required on each fume hood /gas cabinet (ex. digital fpm velocity readout, audible/visual alarm, magnehelic gauge etc.) clearly indicating that the required ventilation airflow rate is being achieved at all times.

-Enclosures need to have an automatic sprinkler system

Additional requirements for <u>above</u> maximum allowable quantities:

-Interlocking the ventilation airflow monitor with an automatic gas shut-off system.

Gas Cabinets: No more than three cylinders are allowed per cabinet, unless each are 1 lb or less.

Small access doors can be used to minimize exhaust volume to provide higher airflow velocity.

If the airflow monitor light is red or if the retest due date on the maintenence sticker is expired, usage should stop.

Treatment Systems

Treatment systems for exhausts of enclosures must be designed to:

a. Handle maximum anticipated pressure of release and sized to process the worst case release
b. Reduce the maximum discharge concentration to 1/2 IDLH of the gas, if there is more than one type of gas in the enclosure, it must be designed to handle the MOST severe case.

Labs may bypass the treatment system requirement if <u>all three</u> of the folllowing conditions are met:
1. Valve outlet plugs are equipped with gas-tight outlet plugs or caps
2. Hand-wheel operated valves have handles that prevent movement
3. Approved containment vessels are provided and are capable of containing a worst case release- such vessels must be moveable to the leaking cylinder.

[1]**Note:** *This is an exception to "normal" use fume hoods which are required to be at a min of 100 fpm with an average of 70.*

Engineering Controls: Gas Detection System[1]	*Alarm priority installations should be given to gases with poor warning properties, odor thresholds above PEL, processes running outside of exhausted enclosures or gases used for long term projects.* ***A detection system is defined to compromise both a monitoring system and linked alarms.***
	Alarm set points should be set as follows (where required): -Inside exhausted enclosures: **IDLH level of the gas** -At discharge of treatment system: **1/2 IDLH of the gas** -Ambient/breathing air locations: **1/2 PEL level of the gas**
	Gas monitoring/alarm systems should have audible and visible alarms in ALL of the following : (1) Gas supply location, (2) Gas use or operator room, and/or (3) Outside of the gas use or storage room (i.e. hallway corridor) The gas detection system should send an alarm, distinct from all other alarms, to a **constantly attended location, unless there is only one cylinder in the lab (only exception).**
Shut-off System & Emergency Power Source	**Automatic shut-off** at the source should occur following detection by the monitoring system. Conditions that prompt automatic shut-down include but are not limited to: any hazardous condition, seismic disturbance, loss of power, loss of ventilation, cooling etc. Emergency shut-off buttons/controls should be clearly labeled. **Valve Shut-off (closure)** should also be automatic. ***Exception:*** *Automatic* shut-off is not required if these 3 conditions are met: 1. Gas is operated at less than 15 pounds per square inch (103.4 kPa). 2. Constantly attended operation. 3. Supply is provided with accessible emergency shut-off valves.
	Emergency Power Source: In the event of a power failure, all of the following should continue to operate without interruption or gas systems should ***automatically shut down at the source:*** 1. Exhaust Ventilation — 4. Gas Detection System 2. Treatment System — 5. Fire Alarms 3. Temperature Control System — 6. Emergncy Alarms Power connections, control switches, and adjustments affecting operation should be protected from direct access by locks on the enclosures.
	Highly Toxic Gases & Pyrophoric: Rooms and enclosures need to have an **automatic fire detection** system that activates a local alarm, subject to approval from the Campus Fire Marshal.
Contact Interactions & Precautions	All regulators, valves, and lines must be constructed of chemically compatible metals. Regulators should be compatible with the size, type and pressure of the cylinder. See Appendix Table A3 or contact the vendor. Regulators and tubing used with oxidizing gases should be cleaned to remove oil, grease, and other reducing agents to prevent the possibility of an explosion oxidizer. Valves of corrosive gas cylinders should be inspected for corrosion and not used if corroded. The vendor must be notified about any damage to a cylinder before return.
	Gas supply lines must be designed with a minimum number of fittings, as each fitting is a potential point of leakage. Some set-ups may require single piping or welded joint lines.
	A check valve or suitable trap must be used when discharging gas into a liquid to prevent the liquid from coming back into the cylinder or regulator.
	Connections infrequently used should be safely disconnected after purging the gas line. If a threaded gas connection in the lab presents a possibility of a leak, then some type of local exhausted enclosure may be needed at the potential leakage point. Consult EH&S.
	Flow restrictors, such as RFOs, should be used to prevent a sudden large gas release.

[1] A gas detection system is not required for a toxic gas that has a physiological warning threshold level below the established PEL.

VII. Reporting Requirements

Reporting any mishap, accident or occurrence with toxic gases as follows:

Event or Trigger	Procedure	Report To…
Missing cylinder	Report Immediately	Principal Investigator EH&S and/or Campus Police
Accidental Gas Release	Close Enclosure if possible; Evacuate and pull fire alarm	Principal Investigator/ Lab Supervisor/Lab members/ EH&S

VIII. Training Requirements and Competency Assessment

All training requirements are outlined in the "Responsibilities" chapter. *Lab Safety Fundamentals* training must be renewed every three years through UCLC. For toxic gas specific training, the PI must decide when the researcher is adequately trained to independently handle toxic gases in the lab. Training should be renewed under the following conditions:

- Changes in the workplace render previous training obsolete
- Changes in the types of cylinder systems or equipment used render previous training obsolete
- Inadequacies in an employee's knowledge of compressed gas cylinders or equipment or observed behavior indicate that the employee has not grasped the required training

IX. Emergency Response Guidelines

All laboratories must have an emergency response plan addressing accidental releases and emergency response to toxic gases. The severity of release events will be affected by several factors including gas concentrations, safety controls such as restrictive flow orifices on the cylinder, the amount of local exhaust and general dilution ventilation in the room. Certain gases have good warning properties that indicate a leak. Examples include anhydrous ammonia (i.e., noticeable irritation) and methyl mercaptan (i.e., noticeable odor). Other gases have poor warning properties such as hydrogen sulfide, which is initially smelled but later causes olfactory fatigue or carbon monoxide (odorless).

In the event of an accidental toxic gas release, the emergency procedures outlined in the UCI Emergency Action Plan should be implemented. If the toxic gas release or leak cannot be stopped quickly by safely closing the cylinder valve, then Emergency # 911 should be called (from a safe location), and the caller should provide the dispatcher with the name of the gas and the release location.

Only trained emergency response personnel with proper personal protective equipment (i.e., SCBAs, Level A suits for gases with a Cal/OSHA Skin notation) and appropriate gas monitoring instruments should be allowed to enter the toxic gas release area.

The following steps should be taken following a toxic gas release:

1. The fire alarm must be activated; the toxic gas release area and the building must be evacuated immediately. The lab PI and EH&S must also be notified immediately.
2. The hazardous area or room shall be barricaded with Caution tape (EH&S/emergency responders) and warning signs to prevent entry by unauthorized personnel. Any doors in the area should be closed, if it is safe to do so.
3. The Safety Data Sheet (SDS) and the Emergency Response Guide (ERG-published by DOT) that applies to the specific toxic gas must be followed.
4. The ERG #'s that apply to the UCI gases include 116, 119, 121, 122, 124, 125, 126, and 139. They state to shut down operations (if safe to do so), ventilate area, control ignition sources, and evacuate area for a minimum distance of several hundred feet.

Personnel Exposure

If personnel exposure to the toxic gas occurs through any physiological route, the gas-specific medical first aid (obtained from the SDS) should be followed immediately. These procedures might include one or more of the following actions:

1. Removal of the exposed person to fresh air if it is safe to do so.
2. Administration of artificial respiration if necessary, by trained personnel.
3. Removal of contact lenses if necessary.
4. Flushing of the eyes with water from an emergency eyewash for 15 minutes.
5. Removal of contaminated clothing and shoes.
6. Flushing of the exposed skin with water from an emergency shower for 15 minutes.
7. Additionally:
   - The information in the UC Irvine Injuries and Medical Treatment poster should also be followed. (http://www.ehs.uci.edu/MedEmergPoster.pdf). In all cases of personnel exposure to a toxic gas, follow-up medical evaluation and care must be provided. EH&S can be contacted for proper arrangements.
   - All serious injuries must be reported to EH&S at x46200 within 8 hours, and an on-line incident report must be completed. (https://www.ehs.uci.edu/apps/hr/index.jsp)

X. Information and External References

The following are regulatory references and standards that govern the handling, use and storage of toxic gases presented in this program:

1. California Fire Code (CFC) 2013
2. Cal/OSHA safety requirements covered in the following sections:
   Section 4650 – Storage, Handling, and Use of Cylinders
   Section 5154.1 – Ventilation Requirements for Laboratory-Type Hood Operations
   Section 5155 – Airborne Contaminants, & PEL Table AC-1
   CCR 8, Section 5191 – Occupational Exposure to Hazardous Chemicals in Laboratories
   CCR 8, Section 5194 – Hazard Communication
3. International Standard BS ISO 10298:2010, ISO 10156:2010

XI. Appendix: Definitions and References

Action Level (AL) – The Cal/OSHA 8-hour Time-Weighted Average (TWA) concentration of an airborne chemical contaminant measured in an employee's breathing zone that triggers certain employer actions, such as training and medical surveillance.

Ceiling Limit (CL) – The Cal/OSHA maximum (peak) concentration of an airborne chemical contaminant measured in an employee's breathing zone that should not be exceeded at any time during the workday.

Compressed Gas – A hazardous material that is stored and shipped in a compressed gas cylinder, is used and handled as a gas, and acts as a gas upon release at normal temperature and pressure. In addition to the chemical hazards of compressed gases, hazards accompanying high pressure or low temperature may also be present due to the physical state of the gas (i.e., liquefied or non-liquefied).

Compressed Gas Association (CGA) Valves – The CGA publishes selection charts or guidelines on which valve connections or fittings to use for specific gases, broken down into both pure and mixed gases. In the United States, these valve connections are commonly referred to as "CGA connections".

Department of Transportation (DOT) – The federal agency in the United States responsible for promulgating and enforcing safety regulations to control the commercial transportation of hazardous materials, including toxic, pyrophoric, and other hazardous compressed gases.

Diameter Index Safety System (DISS) Valves – A specific type of CGA cylinder outlet valve connection that is generally used where the highest gas purity and the lowest leak rate connections are required. Various toxic and corrosive gases are assigned different DISS-CGA valve connections that provide a metal-to-metal seal.

Exhausted Enclosures – Include locally ventilated gas cabinets and fume hoods.

UCI Toxic Gas Program

Gas – One of the three main states of matter that is composed of molecules in constant random motion. More specifically, flammable and toxic gases are materials that are gases at a temperature of 68° F or less and a pressure of 14.7 psi, or materials that have a boiling point of 68° F or less at a pressure of 14.7 psi.

Health Hazard Gases – Toxic gases that may cause significant acute health effects at low concentrations. The criteria used to establish the list of health hazard gases are: (1) An NFPA health hazard rating of 3 or 4 for a gas that has a LC50 between 0 and 3,000 ppm; (2) An NFPA health hazard rating of 2 for a gas that has poor physiological warning properties; (3) A gas that exhibits pyrophoric (self-igniting) characteristics; or (4) A gas that has extremely low Occupational Exposure Limits (OELs) in the absence of an NFPA health hazard rating.

Highly Toxic Gas – The California Fire Code class for a gas that has a median lethal concentration (LC50) between 0 and 200 parts per million (ppm) by volume in air when administered by continuous inhalation for one hour or less to albino rats, each weighing between 200 and 300 grams (0.44 and 0.66 lbs.).

Immediately Dangerous to Life or Health (IDLH) – An atmospheric concentration of any toxic, corrosive, or asphyxiating substance that poses an immediate threat to life, would cause irreversible or delayed adverse health effects, or would impair or interfere with an individual's ability to escape from a dangerous atmosphere.

Leak Test – Any reliable method used to test a pressurized gas cylinder connection. It may include coating all non-welded joints or connections with a soap solution that is capable of forming bubbles at any gas leak points, a pneumatic pressure leak-down test using accurate pressure gauges, or other effective measures.

Lethal Concentration 50% (LC50) – The airborne concentration (ppm) of a toxic gas that kills 50% of the test animals during a 1-hour exposure period. It is a measure of acute toxicity by the inhalation route of exposure.

Locally Ventilated Enclosure (LVE) – The enclosure and connection of a potential gas leak point (i.e., a threaded gas connection on a piece of research equipment) to a local exhaust ventilation system. It is generally used whenever a toxic or corrosive gas is used in the open room, outside of an exhausted enclosure and has an increased probability of a leak.

Magnehelic Gauge – A differential pressure gauge used for the accurate measurement of air pressure, velocity, and flow, primarily in local exhaust ventilation systems used in exhausted enclosures.

National Fire Protection Association (NFPA) – A United States trade association that develops consensus standards and codes for usage and adoption by federal, state, and local governments. These standards and codes are designed to reduce the risk and effects of fire by establishing design, installation, and service criteria for buildings, processes, and materials

Permissible Exposure Limit (PEL) – The Cal/OSHA 8-hour Time-Weighted Average (TWA) concentration of an airborne chemical contaminant measured in an employee's breathing zone that should not be exceeded when averaged over an 8-hour workday

Pyrophoric Gas – A gas that, upon contact with air or oxygen, will ignite spontaneously at or below a temperature of 54.5 degrees C (130 degrees F)

Restrictive Flow Orifice (RFO) – An in-line cylinder device that reduces the maximum gas release rate

Risk Management and Prevention Program (RMPP) – A RMPP is required by Cal/EPA to anticipate and prevent circumstances that could result in accidental releases of Acutely Hazardous Materials (AHMs) if used in amounts greater than the Threshold Planning Quantities (TPQs), in pounds

Short-Term Exposure Limit (STEL) – The Cal/OSHA 15-minute Time-Weighted Average (TWA) concentration of an airborne chemical contaminant measured in an employee's breathing zone that should not be exceeded for any 15-minute period during the workday, even if the 8-hour Time-Weighted Average concentration is below the Permissible Exposure Limit

Standard Temperature and Pressure (STP) – STP corresponds to 273° Kelvin (0° Celsius) and 1 atmosphere pressure. It is often used for measuring gas density and volume.

Threshold Limit Value (TLV) –The ACGIH 8-hour Time-Weighted Average (TWA) concentration of an airborne chemical contaminant measured in an employee's breathing zone that nearly all workers may be repeatedly exposed to, day after day for a 40-hour work week over a working lifetime, without experiencing adverse toxic health effects.

Toxic Gas – The California Fire Code class for a gas that has a median lethal concentration (LC50) between 201 and 2,000 ppm by volume in air when administered by continuous inhalation for one hour or less to albino rats, each weighing between 200 and 300 g (0.44 and 0.66 lbs.).

Inward face velocity- Average linear air velocity into the exhaust system measured at the opening into the hood

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Table A1: Hazardous Gas Classification Table

Table A1 shows how the CFC toxic gas classes compare to the NFPA health hazard classes. UCI follows the CFC system.

Toxic & Health Hazard Gas Classes					
Pure Gas LC50 (ppm)	0-200	201-1,000	1,001-2,000	2,001-3,000	3,001-5,000
CFC Toxic Gas Classes	Highly Toxic	Toxic		N/A	
NFPA Health Hazard Classes	4		3		2

Table A2: Toxic & Highly Toxic Gas List

Table A2 includes toxic compressed gases that fall into CFC toxic and highly toxic categories. Other hazardous compressed gases (i.e., asphyxiants, flammable gases, oxidizers etc.) are not included in this table but are regulated by the compressed gas program. The highlighted gases are ones currently present on the UCI Campus.

Name/ Molecular Formula	CAS, UN/NA #	UBC/CFC Class[1]	IDLH[2]	LC50[3]	PEL[4]
Ammonia – NH_3	7664–41–7, UN1005	Toxic, Corrosive	300 ppm	7,338 ppm	25 ppm TWA 35 ppm STEL
Arsine – AsH_3	7784–42–1, UN2188	Highly Toxic, Flammable, Pyrophoric	3 ppm	178 ppm	0.05 ppm TWA
Boron Tribromide – BBr_3	10294–33–4, UN2692	Toxic, Corrosive	50 ppm	380 ppm	1 ppm CL
Boron Trichloride – BCl_3	10294–34–5, UN1741	Toxic, Corrosive	25 ppm	2,541 ppm	1 ppm CL
Boron Trifluoride – BF_3	7637–07–2, UN1008	Toxic, Corrosive	25 ppm	864 ppm	1 ppm CL
Bromine – Br_2	7726–95–6, UN1744	Highly Toxic, Corrosive, Oxidizer	3 ppm	113 ppm	0.1 ppm CL
Carbon Monoxide – CO	630–08–0, UN1016	Toxic, Flammable	1,200 ppm	3,760 ppm	25 ppm TWA 200 ppm CL
Chlorine – Cl_2	7782–50–5, UN1017	Toxic, Corrosive, Oxidizer	10 ppm	293 ppm	0.5 ppm TWA 1 ppm STEL
Chlorine Dioxide – ClO_2	10049–04–4, NA9191	Toxic, Oxidizer	5 ppm	250 ppm	0.1 ppm TWA 0.3 ppm STEL
Chlorine Trifluoride – ClF_3	7790–91–2, UN1749	Toxic, Oxidizer, Corrosive	20 ppm	299 ppm	0.1 ppm CL
Diborane – B_2H_6	19278–45–7, UN1911	Highly Toxic, Flammable, Pyrophoric	15 ppm	80 ppm	0.1 ppm TWA
Dichlorosilane – SiH_2Cl_2 (HCl)	4109–96–0, UN2189	Toxic, Corrosive, Flammable, Pyrophoric	50 ppm	314 ppm	5 ppm CL
Ethylene Oxide – C_2H_40	75–21–8, UN1040	Toxic, Flammable	800 ppm	2,900 ppm	1 ppm TWA 5 ppm STEL
Fluorine – F_2	7782–41–4, UN1045	Highly Toxic, Corrosive, Oxidizer	25 ppm	185 ppm	0.1 ppm TWA
Germanium Tetrahydride – GeH_4	7782–65–2, UN2192	Highly Toxic, Flammable, Pyrophoric	6 ppm	620 ppm	0.2 ppm TWA
Hydrogen Bromide – HBr	10035–10–6, UN1048	Toxic, Corrosive	30 ppm	2,860 ppm	3 ppm CL
Hydrogen Chloride – HCl	7647–01–0, UN1050	Toxic, Corrosive	50 ppm	2,810 ppm	5 ppm CL
Hydrogen Cyanide – HCN	74–90–8, UN1051	Highly Toxic, Flammable	50 ppm	40 ppm	4.7 ppm CL

Name/ Molecular Formula	CAS, UN/NA #	UBC/CFC Class[1]	IDLH[2]	LC50[3]	PEL[4]
Hydrogen Fluoride – HF	7664–39–3, UN1052	Toxic, Corrosive	30 ppm	1,300 ppm	0.4 ppm TWA 1 ppm STEL
Hydrogen Selenide – H_2Se	7783–07–5, UN2202	Highly Toxic, Flammable	1 ppm	51 ppm	0.05 ppm TWA
Hydrogen Sulfide – H_2S	7783–06–4, UN1053	Toxic, Flammable, Corrosive	100 ppm	712 ppm	10 ppm TWA 15 ppm STEL 50 ppm CL
Methyl Bromide – CH_3Br	74–83–9, UN1062	Toxic, Flammable	250 ppm	850 ppm	1 ppm TWA 20 ppm CL
Methyl isocyanate – CH_3NCO	624–83–9, UN2480	Highly Toxic, Flammable	3 ppm	22 ppm	0.02 ppm TWA
Methyl Mercaptan – CH_3SH	74–93–1, UN1064	Toxic, Flammable	150 ppm	1,350 ppm	0.5 ppm TWA
Nickel Carbonyl – $Ni(CO)_4$	13463–39–3, UN1259	Highly Toxic, Flammable	2 ppm	18 ppm	0.001 ppm TWA
Nitric Oxide – NO	10102–43–9, UN1660	Highly Toxic, Oxidizer, Corrosive	100 ppm	115 ppm	25 ppm TWA
Nitrogen Dioxide – NO_2	10102–44–0, UN1067	Highly Toxic, Oxidizer, Corrosive	20 ppm	115 ppm	1 ppm STEL
Ozone – O_3	10028–15–6, UN1955	Highly Toxic, Oxidizer	5 ppm	9 ppm	0.1ppm TWA 0.3 ppm STEL
Phosgene – $COCl_2$	75–44–5, UN1076	Highly Toxic	2 ppm	5 ppm	0.1 ppm TWA
Phosphine – PH_3	7803–51–2, UN2199	Highly Toxic, Flammable, Pyrophoric	50 ppm	20 ppm	0.3 ppm TWA 1 ppm STEL
Phosphorus Oxychloride – $POCl_3$	10025–87–3, UN1810	Highly Toxic	1 ppm	96 ppm	0.1 ppm TWA
Phosphorus Pentafluoride – PF_5	7647–19–0, UN2198	Toxic, Oxidizer, Corrosive	2.61 ppm	261 ppm	1 ppm STEL (as HF)
Phosphorus Trichloride – PCl_3	7719–12–2, UN1809	Toxic, Corrosive	25 ppm	208 ppm	0.2 ppm TWA 0.5 ppm STEL
Selenium Hexafluoride – SeF_6	7783–79–1, UN2194	Highly Toxic, Corrosive	2 ppm	50 ppm	0.05 ppm TWA (as Se)
Silicon Tetrahydride (Silane)– SiH_4	7803–62–5, UN2203	Pyrophoric, Flammable	100 ppm	19,000 ppm	5 ppm TWA
Silicon Tetrachloride – $SiCl_4$	10026–04–7, UN1818	Toxic, Corrosive	100 ppm	750 ppm	5 ppm CL (as HCl)
Silicon Tetrafluoride– SiF_4	7783–61–1, UN1859	Toxic, Corrosive	30 ppm	922 ppm	1 ppm STEL (as HF)
Stibine – SbH_3	7803–52–3, UN2676	Highly Toxic, Flammable	5 ppm	178 ppm	0.1 ppm TWA
Sulfur Dioxide – SO_2	7446–09–5, UN1079	Toxic, Corrosive	100 ppm	2,520 ppm	2 ppm TWA 5 ppm STEL
Sulfuryl Fluoride – SO_2F_2	2699–79–8, UN2191	Toxic, Corrosive	1,000 ppm	3,020 ppm	5 ppm TWA 10 ppm STEL
Tellurium Hexafluoride – TeF_6	7783–80–4, UN2195	Highly Toxic, Corrosive	1 ppm	25 ppm	0.02 ppm TWA (as Te)
Titanium Tetrachloride	7550-45-0 UN1838	Highly Toxic Corrosive	1.3 ppm	119 ppm	
Tungsten Hexafluoride – WF_6	7783–82–6, UN2196	Toxic, Corrosive	30 ppm	218 ppm	1 ppm STEL (as HF)
Xenon Difluoride, XeF_2	13709-36-9	Toxic, Corrosive, Oxidizer	250 ppm	445 ppm	2.5ppm TWA

Table A3: Material Compatibility Chart

Toxic & Flammable/Pyrophoric — *Toxic/Flammable or Toxic/Pyrophoric gases are to be labeled with yellow background over black font.*

	Metal						Non-Metal			
	Stainless Steel-316/304	Monel (Cu/Ni)	Brass	Aluminum	Copper	Zinc	Tygon (PVC)	Teflon	Neoprene	Viton
Arsine	C/I	C	C	-	C	-	C	C	C	C
Carbon Monoxide	C/ C	C	C	C	C	C	C	C	C	C
Diborane	C/C	C	C	C	C	-	-	-	-	-
Dichlorosilane	C/C	C	-	-	-	-	-	C	-	-
Disilane	C/C	C	C	C	C	-	-	C	C	C
Hydrogen Sulfide	C/C-*less*	C	I	C	-	-	C	C	C	I
Methyl Bromide	C/ C	-	C	I	C	-	I	-	I	C
Methyl Mercaptan	C/C	C	C	C	C	-	-	-	-	-
Phosphine	C/ C	C	-	C	-	-	I	-	-	-
Silane (Silicon Tetrahydride)	C/C	C	C	C	C	-	-	C	C	C

Toxic & Corrosive — *Toxic/Corrosive gases are to be labeled with orange background over black font.*

	Metal						Non-Metal			
	Stainless Steel-316/ 304	Monel (Cu/Ni)	Brass	Aluminum	Copper	Zinc	Tygon (PVC)	Teflon	Neoprene	Viton
Ammonia, Liquid	C/ C	C	I	C	I	I	C	C	C	I
Ammonia, Anhydrous	C/ C	C	I	C	I	I	C	I	C	I
Boron Trichloride	C/ -	C	E	I	C	-	-	C	-	-
Boron Trifluoride	C/	C	E	C	E	-	-	C	-	-
Bromine	I/I	C	-	I	-	-	C-*less*	C	I	C
Chlorine	C/ C	C	I	I	I	I	C	C	I	C
Fluorine	C/ C-*less*	C	E	E	E	E	I	E	I	I
Hydrogen Bromide/	C/I	C	I	I	I	I	C	C	I	C
Hydrogen Chloride	I/I	C	I	I	I	I	C	C	I	C
Hydrogen Fluoride	C/I	C	I	I	I	-	-	C	I	I
Nitric Oxide	C/ C	C	I	C	C	-	C	-	C	-
Nitrogen Dioxide	C/ C	C	I	C	I	I	I	C	I	I
Sulfur Dioxide	C/ I	C	I	C	C	I	C	C	I	C
Sulfur Hexafluoride	C/ C	C	C	C	C	I	C	C	C	C
Xenon Difluoride	*See manufacturer's specifications*									

C- Excellent or good *compatibility, C-less-fair compatibility*
I- *Incompatible*
E- *Exceptions for compatibility, consult manufacturer*
- - *Not determined*

Precautionary Notes:

- Investigate other conditions that may affect compatibility such as temperature & pressure (data at room temperature).
- Always check manufacturer's recommendations for pipe and tube use and specifications. Experimental variables such as temperature rating, pressure, certain processes etc. and <u>may shorten the expected lifetime of the pipe/tube</u>.
- Different grades of stainless steel can affect the compatibility.
- Stainless 304 and 316 are the most commonly used in labs, 316 is always a better choice than 304 as it is more chemically resistant (Molybdenum-doped). If using another grade, compatibility should be investigated prior to use.

Footnotes for Table A2:

1. Uniform Building Code (UBC) / 2010 California Fire Code (CFC) Class, Highly Toxic = 0-200 ppm LC50, Toxic = 201-2,000 ppm LC50, Physical hazards per CFC Standard 7903
2. Immediately Dangerous to Life or Health (IDLH) Concentrations, NIOSH, and Threshold Limit Values (TLV) and Immediately Dangerous to Life and Health (IDLH) Values, Matheson Tri-Gas
3. LC50 data: Lowest reported value, 1 hour adjusted, Department of Transportation, Compressed Gas Association, and Registry of Toxic Effects of Chemical Substances, Canadian Centre for Occupational Health and Safety
4. Table AC-1 Permissible Exposure Limits (PELs) for Chemical Contaminants, California Department of Industrial Relations (DIR), Cal-OSHA, California Code of Regulations (CCR), Title 8, Section 5155, American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Values (TLVs), 2013 booklet