

Appendix D: Toxic and highly toxic gases

Toxic and highly toxic gases may cause significant acute health effects at low concentrations. Health effects may include severe skin or eye irritation, pulmonary edema, neurotoxicity, or other potentially fatal conditions. The criteria used to establish the materials addressed by this program are:

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

Table 1 identifies common gases that meet the criteria of toxic or highly toxic, though it is not exhaustive.

Table 1 – Common Toxic and Highly Toxic Gases

| | | |
|-----------------------|-----------------------------|-----------------------------|
| allene | Dichlorosilane | nitric oxide |
| ammonia | Dimethylamine | nitrogen dioxide |
| arsenic pentafluoride | Disilane | nitrogen trifluoride |
| arsine | Fluorine | phosgene |
| boron trichloride | fluorine mixtures | phosphine |
| boron trifluoride | germane (GeH ₄) | phosphorous pentafluoride |
| bromine pentafluoride | hydrogen bromide | phosphorous trichloride |
| bromine trifluoride | hydrogen chloride | phosphorous trifluoride |
| 1,3 butadiene | hydrogen cyanide | silicon tetrafluoride |
| carbon tetrafluoride | hydrogen fluoride | stibene (SbH ₃) |
| carbon monoxide | hydrogen selenide | sulfur tetrafluoride |
| carbonyl sulfide | hydrogen sulfide | sulfuryl fluoride |
| chlorine | methyl bromide | tungsten hexafluoride |
| chlorine trifluoride | methyl chloride | vinyl chloride |
| cyanogen | methyl silane | |
| cyanogen chloride | Monomethylamine | |
| diborane | nickel carbonyl | |

Certain dilute toxic gases are exempt from this program if worst case release modeling of an accidental acute release indicates that the gas concentrations will not result in exposures to laboratory personnel exceeding any of the following:

- The OSHA Short Term Exposure Limit (STEL)
- The Threshold Limit Value-ceiling (TLV-C)
- Any recognized full shift exposure standard if there is no STEL or TLV-C for the material
- One half of the concentration established as Immediately Dangerous to Life or Health (IDLH)

ALL exemptions on the basis of dilution will be made on a case-by-case basis by the Office of the Environmental Health & Safety (EHS).

Exposure Control Methods

A. Engineering Controls

For personnel and environmental protection against the potential exposure to toxic and highly toxic gases, the following engineering controls are required:

1. All toxic and highly toxic gas cylinders and reaction vessels/chambers shall be kept and used in a chemical fume hood, gas cabinet or exhausted enclosure that meets the following minimum requirements:

Fume hoods shall:

- Be certified for chemical use by EHS within the last year (as indicated by a certification sticker on the fume hood)
- Be used for all manipulations. If the use of a fume hood is impractical, other ventilations shall be provided
- Have airflow measuring devices and visual and audible alarms that signify low airflow conditions
- Be located in rooms that are exhausted and negative in pressure to surrounding areas.

Gas cabinets shall:

- Be located in rooms that are exhausted and operate at negative pressure in relation to surrounding areas
- Have self-closing limited access ports or non-combustible windows to give access to equipment controls
- Provide an average velocity at the face of access ports or windows not less than 200 feet per minute with a minimum of 150 feet per minute at any point (call EHS @ 951-827-5528 to have air flows measured)
- Be connected to an exhaust
- Have self-closing doors
- Be sprinkled
- Be constructed of not less than 12 gauge steel
- Have airflow measuring devices and visual and audible alarms that signify low airflow conditions
- Be installed through the Facilities or vendor.

Exhausted enclosures shall:

- Operate at negative pressure in relation to surrounding areas;
- Provide an average velocity at the face of access ports or windows not less than 200 feet per minute with a minimum of 150 feet per minute at any point (call EHS @ 951-827-5528 to have air flows measured);
- Have airflow measuring devices and visual and audible alarms that signify low airflow conditions
- Be located in rooms that are exhausted and negative in pressure to surrounding areas

2. All exhaust lines or ducts carrying purged or exhausted emissions of toxic gases must be connected to a mechanical exhaust system that discharges to a safe location (i.e. presents no potential for re-entrainment into any building supply air intake or occupied area). Exhaust wall ducts shall be chemically resistant to degradation by the toxic gas in use.

B. Work Practice Controls

For personnel and environmental protection against the potential exposure to toxic and highly toxic gases, the following work practice controls should be used:

Handling:

The following work practice controls must be used when handling toxic and highly toxic gases:

- Safety Data Sheets (SDS) must be reviewed prior to working with any toxic or highly toxic gas
- Standard Operating Procedures (SOP) must be developed for the gas(es) in use

At a minimum, SOPs shall contain:

- Safety precautions for the storage, handling and use/delivery of the gases
 - Identification of all PPE that will be worn
 - Description of toxic gas monitoring systems
 - Emergency response procedures
 - Consult EHS (951-827-5528) for SOP review and/or development
- All cylinders shall be immediately leak tested with a leak indicating solution and must be clearly labeled with content and hazard information
 - All work with toxic or highly toxic gases must be conducted in a working chemical fume hood to prevent exposure by inhalation
 - Proper personal protection equipment (PPE) must be worn at all times to prevent eye and skin contact
 - No work with toxic or highly toxic gases shall be performed alone
 - Do not drag, roll, slide or drop cylinders. A suitable hand truck, to which the cylinder is secured, must be used for cylinder movement.

- When transporting gases outside the lab, the protective cap shall be in place and shall cover the valve.
- Never attempt to lift a cylinder by its cap.
- Secure cylinders at all times while in use and during transport.
- Only use approved regulators and valves. Consult your gas supplier for approved regulators and valves.
- Once cylinder has been connected to process, open valve slowly and carefully. If experiencing difficulty opening cylinder valve, discontinue use and contact supplier. Forced freeing of “frozen” or corroded valves should NOT be attempted.
- Regulators and valves should be kept free of moisture. Systems should be purged with dry inert gas (e.g. helium, nitrogen, argon, etc.) before the product is introduced and when system is out of service.
- The main valve on all toxic and highly toxic gas cylinders must be closed at all times when the cylinder is not in use

In addition to protocol for hazardous gases piping and tubing [section 14](#), toxic and highly toxic gases shall:

- be identified to indicate the material conveyed and arrows shall indicate the direction of flow
- have readily accessible manual or automatic remotely activated fail-safe emergency shutoff valves installed on supply tubing at the point of use and the source
- have emergency shutoff valves identified and the location shall be clearly visible and indicated by means of a sign
- have backflow-prevention or check valves when backflow of hazardous materials could create a hazardous condition of caused the unauthorized discharge of hazardous materials
- have excess flow control when gas is carried in pressurized piping above 15 psi. The excess flow control shall be located in the source exhausted enclosure

Disposal:

The following work practice controls must be used when disposing of toxic and highly toxic gas cylinders:

- All empty toxic and highly toxic gas cylinders shall be labeled as empty
- Toxic gases should only be purchased by vendors who will agree to take back the empty cylinder
- Any cylinders that will or cannot be removed by the vendor must be disposed of through EHS.

C. Personal Protective Equipment

For personnel and environmental protection against the potential exposure to toxic and highly toxic gases the following personal protective equipment should be used by personnel:

- laboratory coats or gowns must be worn at all times in the toxic or highly toxic gas area
- Appropriate hand protection must be used when handling toxic and highly toxic gases
- Safety goggles must be worn at all times in the toxic or highly toxic gas area
- When employee exposure exceeds the Permissible Exposure Limit (PEL) or Threshold Limit Value (TLV) (whichever is lower), respiratory protection will be required.

NOTE: Personnel must be enrolled in EHS Respiratory Protection program before wearing respiratory protection. To enroll please contact EHS Industrial Hygienist x22964

D. Toxic Gas Monitors

Electronic toxic gas monitors shall be installed and continuously operated whenever a toxic or highly toxic gas is used or stored. All gas monitoring systems shall have:

- Audible and visible alarms located in gas supply locations, gas use locations, and outside the gas use room
- An alarm status and gas concentration readout panel located outside the gas room;
- Local audible and visual alarms specific and distinct from fire alarm bells. The alarm's sound should be significant in meaning and require personnel action
- The toxic gas alarm level set-point set at the Permissible Exposure Limit (PEL) or Threshold Limit Value (TLV), whichever is lower
- Connection to an emergency power source
- Locks or enclosures that protect power connections and control switches that affect the detection system operation.