Scope and Background

The Carnegie Mellon University Toxic and Highly Toxic Gas Handling Program specifies minimum requirements for safe storage, use, and handling of toxic and highly toxic gas at Carnegie Mellon University. This program has been approved by the Laboratory Safety Committee.

This document:
- summarizes the health and safety risks associated with toxic and highly toxic gas use and handling;
- identifies exposure control methods to protect employee’s safety and health and the environment;
- outlines regulatory and university requirements related to this work;
- specifies emergency response procedures for addressing toxic gas issues; and
- provides resources for further information.

Toxic and highly toxic gases are gases that 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 policy 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.

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 Carnegie Mellon’s Environmental Health & Safety (EH&S) department.

Training

In accordance with federal, state, and institutional regulations and policies, all persons using toxic at Carnegie Mellon University must complete training before they are eligible to work with toxic and highly toxic gases. All personnel working with toxic and highly toxic gases must complete the proper training prior to their first contact with these materials. For information on how to receive the necessary training, visit this location: [http://www.cmu.edu/ehs/training/index.html](http://www.cmu.edu/ehs/training/index.html) and select “Compressed Gas and Toxic Gas Procedures.”
Table 1 – Common Toxic and Highly Toxic Gases

<table>
<thead>
<tr>
<th>allene</th>
<th>dichlorosilane</th>
<th>nitric oxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>ammonia</td>
<td>dimethylamine</td>
<td>nitrogen dioxide</td>
</tr>
<tr>
<td>arsenic pentafluoride</td>
<td>disilane</td>
<td>nitrogen trifluoride</td>
</tr>
<tr>
<td>arsine</td>
<td>fluorine</td>
<td>phosgene</td>
</tr>
<tr>
<td>boron trichloride</td>
<td>fluorine mixtures</td>
<td>phosphine</td>
</tr>
<tr>
<td>boron trifluoride</td>
<td>germane (GeH₄)</td>
<td>phosphorous pentafluoride</td>
</tr>
<tr>
<td>bromine pentafluoride</td>
<td>hydrogen bromide</td>
<td>phosphorous trichloride</td>
</tr>
<tr>
<td>bromine trifluoride</td>
<td>hydrogen chloride</td>
<td>phosphorous trifluoride</td>
</tr>
<tr>
<td>1,3 butadiene</td>
<td>hydrogen cyanide</td>
<td>silane (SiH₄)</td>
</tr>
<tr>
<td>carbon tetrafluoride</td>
<td>hydrogen fluoride</td>
<td>silicon tetrafluoride</td>
</tr>
<tr>
<td>carbon monoxide</td>
<td>hydrogen selenide</td>
<td>stibene (SbH₃)</td>
</tr>
<tr>
<td>carbonyl sulfide</td>
<td>hydrogen sulfide</td>
<td>sulfur tetrafluoride</td>
</tr>
<tr>
<td>chlorine</td>
<td>methyl bromide</td>
<td>sulfuryl fluoride</td>
</tr>
<tr>
<td>chlorine trifluoride</td>
<td>methyl chloride</td>
<td>tungsten hexafluoride</td>
</tr>
<tr>
<td>cyanogen</td>
<td>methyl silane</td>
<td>vinyl chloride</td>
</tr>
<tr>
<td>cyanogen chloride</td>
<td>monomethylamine</td>
<td></td>
</tr>
<tr>
<td>diborane</td>
<td>nickel carbonyl</td>
<td></td>
</tr>
</tbody>
</table>

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 used for all manipulations. If the use of a fume hood is impractical, other ventilations shall be provided. Fume hoods shall:
   - Be certified for chemical use by EH&S within the last year (as indicated by a certification sticker on the fume hood).
   - 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:
   - 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;


Page 2 of 5

Toxic and Highly Toxic Gas Handling Program

November 13, 2012
• Provide and average velocity at the face of access ports or windows not less that 200 feet per minimum with a minimum of 150 feet per minute at any point (call EH&S at 412-268-8411 to have air flows measured);
• Be connected to an exhaust;
• Have self-closing doors;
• Be constructed of not less than 12 gauge steel
• 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
• Be installed through the department of Campus Design and Facility Development (CDFD).

Exhausted enclosures shall:
• Operate at negative pressure in relation to surrounding areas;
• Provide and average velocity at the face of access ports or windows not less that 200 feet per minimum with a minimum of 150 feet per minute at any point (call EH&S at 412-268-8411 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 by personnel:

Handling:
The following work practice controls must be used when handling toxic and highly toxic gases:
• Material Safety Data Sheets (MSDS) 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; the University’s PHS procedure format may be used.
• 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.
Piping, tubing, valves and fittings:
The following must be considered when selecting and using piping, tubing, valves, and fittings for use of toxic or highly toxic gases. Piping, tubing, valves and fittings:

- shall be designed and fabricated from materials compatible with the material to be contained and shall be of adequate length and durability to withstand the pressure and structural stress and exposure to which they are subject
- shall be identified to indicate the material conveyed and arrows shall indicate the direction of flow
- shall 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
- shall have emergency shutoff valves identified and the location shall be clearly visible and indicated by means of a sign
- shall have backflow-prevention or check valves when backflow of hazardous materials could create a hazardous condition or caused the unauthorized discharge of hazardous materials
- shall 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
- shall not be located within corridors, within any portion of a means of egress or in concealed spaces

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

- Cylinders must be stored in a well ventilated area, protected from the weather.
- Cylinders should be stored in locations appropriate for compressed gas storage and separated from incompatible compounds by: a distance of not less than 20 feet: OR a noncombustible partition extending not less than 18 inches above and to the sides of the cylinders.
- Cylinders shall be stored upright with valve protection caps in place.
- Do not allow storage temperature to exceed 125 degrees F.
- Stored cylinders away from heavily traveled areas and emergency exits.
- Visually inspect cylinders on a routine basis, at least weekly, for any indication of leakage or other problems.

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 cannot be removed by the vendor must be disposed of through EH&S.

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:

- Uniforms, gowns or laboratory coats must be worn at all times in the toxic or highly toxic gas area;
- Latex, nitrile, vinyl gloves, or heavy duty rubber gloves 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: You must be enrolled in Carnegie Mellon University’s Respiratory Protection Program before wearing respiratory protection! To enroll in the program contact Mark Banister at 8-1493 or Michael Fouch at 8-3221.
D. Standard Operating Procedures
Principal Investigators are required to ensure that written Standard Operating Procedures (SOPs) are developed for all toxic and highly toxic gases they are using. 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

Standard Operating Procedures must be submitted to EH&S for review and must be approved by EH&S prior to implementing them. Once approved, SOPs must be submitted to the EH&S every three years for periodic review, or when significant changes have been made.

E. 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 and be 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 and sings to indicate the alarm's meaning and required 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.

Emergency Response

- In case of accidental release of a poisonous gas, such as a leaking cylinder, turn off all ignition sources (if time permits), evacuate the area immediately and close the door.
- In the event of personnel skin contamination, wash with soap and water and remove contaminated clothing.
- In the event of personnel eye contamination immediately flush the exposed area using an eye wash or water for 15 minutes.
- In the event of personnel exposure via inhalation, remove to fresh air and
- Call campus police at 8-2323 to arrange for medical attention for exposed personnel and to report the incident.

Note: When medical attention is needed, the MSDS sheet for the toxic or highly toxic gas should be brought to the hospital to assist in treatment.