Minimum Safety Requirements for Toxic, Corrosive and Reactive Compressed Gases

EXPLAINED

CBC Lab Safety Workshop
Beyond the Basics
Wednesday, March 16, 2011
University of Arizona Student Union
Tucson Room

Overview

- Define terms in presentation
- Provide specific gas examples
- Explain need for concern
- Explain general hazard control approach
- Introduce minimum requirements checklist
- Describe an application of requirements
- Campus resources

Toxic and Highly Toxic Gases

- **Toxic:** LC_{50} between 200 and 2000 parts per million *
- **Highly toxic:** LC_{50} of less than 200 parts per million *

* when administered continuously by inhalation for one hour to albino rats

Corrosive Gases

- Gases that cause visible destruction or, or irreversible alterations in, living tissue by chemical action at the site of initial contact

Reactive Gases

- **Unstable (reactive):** Gases which in the pure state, or as produced or transported, will vigorously polymerize, decompose, condense, or will become self-reactive under conditions of shocks, pressure, or temperature

Compressed Gases

- Gases or mixture of gases having, in a container, an absolute pressure exceeding
  - 40 psi at 70°F (21.1°C); a gas or mixture of gases having, in a container, an absolute pressure exceeding OR
  - 104 psi at 130°F (54.4°C) regardless of the pressure at 70°F,
- or a liquid having a vapor pressure exceeding 40 psi at 100°F (37.8°C).

TOXIC, CORROSIVE AND REACTIVE COMPRESSED GASES

(examples)

- **Toxic and Highly Toxic**
  - carbon monoxide
  - arsine
  - chlorine
  - cyanogen chloride
  - diborane
  - fluorine
  - germane
  - phosgene
  - hydrogen cyanide
  - hydrogen fluoride
  - hydrogen selenide
  - hydrogen sulfide
  - nitric oxide
  - nitrogen dioxide
  - phosphine

- **Carcinogenic**
  - 1,3-butadiene
  - vinyl chloride
  - ethylene oxide

- **Corrosive**
  - ammonia
  - chlorine
  - hydrogen fluoride
  - sulfur dioxide
  - silicon tetrafluoride
  - hydrogen chloride
  - hydrogen bromide

- **Reactive**
  - silane
  - germane
  - dichloroborane
  - phosphine
  - stibine

Why the Extra Concern?

- Difficult to contain
  - High vapor pressure (VP)
  - Under pressure
    - e.g., ammonia – 114 psi @70^{o}F
    - e.g., nitric oxide, chlorine, hydrogen cyanide - 2000 psi
- Large quantity in a small package
    - e.g., 50” ammonia cylinder, 50 lbs liquid or 1039 ft^3 gas

Why the Extra Concern?

- Low exposure limit
  - e.g., arsine, hydrogen selenide – 0.05 ppm (TWA)
  - e.g., cyanogen chloride – 0.3 ppm (Ceiling)
  - e.g., fluorine – 2 ppm (Ceiling)
  - e.g., ammonia, carbon monoxide – 25 ppm (TWA)
  - contrast e.g., acetone – 500 ppm (TWA)

Why the Extra Concern?

- High vapor hazard ratio (VHR)
  - VHR = $\frac{\text{(VP @ temperature of use)}(10^6)/\text{atmospheric pressure}}{\text{exposure limit}}$
  - e.g., arsine $\frac{(114\ \text{psi})(10^6)/14.7\ \text{psi}}{0.05} = 155 \times 10^6$
  - contrast e.g. acetone $\frac{(185\ \text{mm Hg})(10^6)/760\ \text{mm Hg}}{500} = 490$

Why the Extra Concern?

- Some have history of serious incidents
  - e.g., silane


  - 6 fatalities from gas cabinet explosions where silane was released unignited into the cabinet (two most recent - Taiwan 2005, India 2007,
  - Other major incidents in China and U.S. in 2009

Why the Extra Concern?

- Some are difficult to detect (i.e., poor warning properties)
  - e.g.,:
    - carbon monoxide
    - sulfuryl fluoride
    - hydrogen sulfide

Serious Hazards Require Serious Controls

- Specified Codes and Regulations
  - International Fire Code (IFC 2006)
  - Occupational Safety & Health Administration (OSHA)
- Accepted Consensus Standards/Industry Practice
  - Compressed Gas Association (CGA)
  - Semiconductor Equipment Manufacturers Institute (SEMI)
  - Gas suppliers
- Redundant controls if a single point failure could result in a significant accident or exposure above the occupational exposure limits (OELs)

Primary Hazard Controls

- Minimizing gas quantity
- Enclosing or isolating the source, distribution system and apparatus in which the gas is used

Passive Hazard Controls (require no power or human intervention after initial installation)

- Ventilation

Active Hazard Control (rely on the presence of power or human intervention to be effective)

Passive Hazard Controls

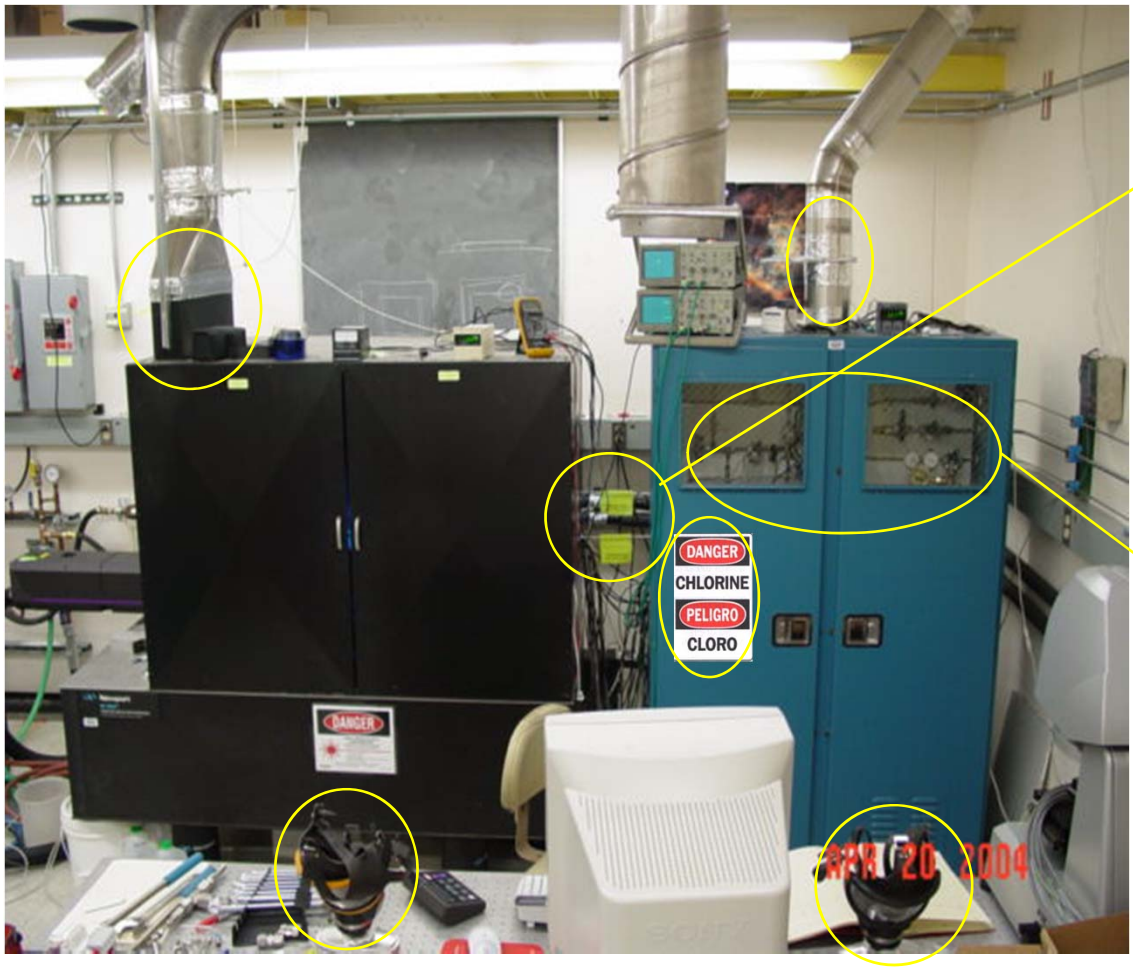
(examples)

- Substitution with non-gaseous compounds
- Dilution in a compatible non-toxic, non-corrosive or non-reactive gas in the cylinder mixed by the vendor (i.e., reduced gas concentration)
- Onsite gas generation
- Quantity limits that can be stored at a given location and used within a reasonable time (i.e., reduced gas amount)
- Restrictive flow orifices (i.e., limited available gas)
- Use of all-welded gas delivery lines (i.e., reduced likelihood of gas leaks)

Active Hazard Controls

(examples)

- Leak testing using an inert gas
- Ventilation with airflow monitor/alarm (regular testing and calibration)
- Operating at pressures below atmospheric
- Gas monitors (regular testing and calibration)
- Process shut-off devices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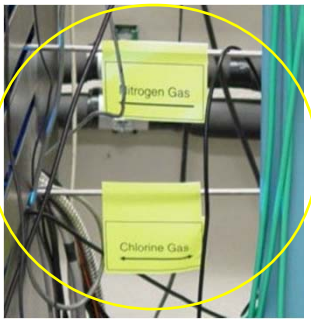
Nitrogen Gas
Chlorine Gas


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408
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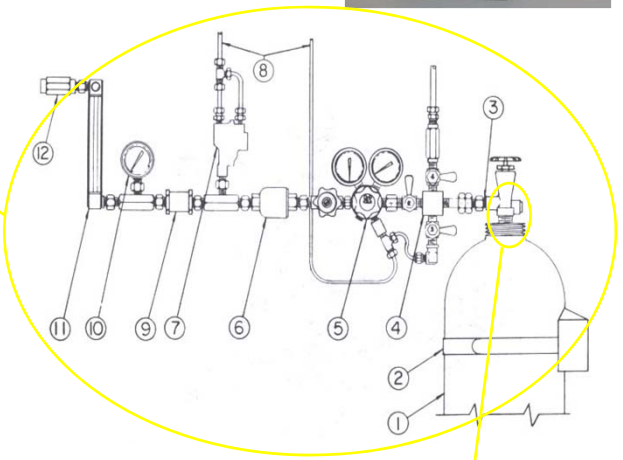
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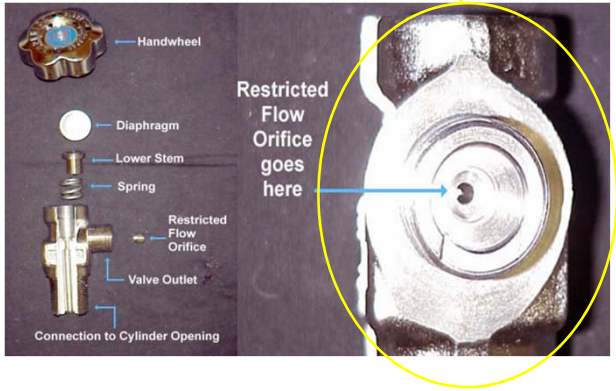
Handwheel
Diaphragm
Lower Stem
Spring
Restricted Flow Orifice
Valve Outlet
Connection to Cylinder Opening
Restricted Flow Orifice goes here

Minimum Safety Requirements Checklist

(http://risk.arizona.edu/healthandsafety/labchemicalsafety/MinReqforCSL-3ToxicCorrosiveGasUse.pdf)

- Quantity limits
- Personal protection and training
- Indoor cylinder location
- Piping, tubing, valves and fittings
- Equipment maintenance
- Environmental protection
- Label, signs and material safety data sheets
- Separation from incompatible materials
- Cylinder handling and transportation
- Security
- Hazard analysis


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ASG
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INHALATION HAZARD
DEC 8 2003


DEC

Carbon Monoxide

- Toxic and flammable compressed gas
- Inhibits the blood from carrying oxygen (brain and heart most susceptible to effects)
- No warning properties
- 76 ft^3/ cylinder, 2000 psi
- Exposure limit = 25 ppm (TWA)
- VHR = 2.3×10^6


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INHALATION HAZARD
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DANGER
Carbon Monoxide
11.10.2010 07:59


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ALARM
AUDIO
TEST
OVERRIDE
MUTE
RESET
11.10.2010 08:00


11.10.2010 08:00


11.10.2010 08:00

Chemical Safety Level 3 (CSL-3) Gases/Gas Activities

- The storage or use of compressed pyrophoric gases in flammable concentrations
- The storage or use of compressed highly toxic gases or compressed toxic gases with poor or no warning properties
- The storage or use of compressed gases, which are select carcinogens, reproductive toxins, toxic or corrosive:
  - in quantities greater than 20 ft^3 OR
  - that are plumbed outside of the source exhausted enclosure
- Transfilling

Need Help?

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