Chemical Process Safety

Chapter 3: Industrial Hygiene

Government Regulations

1. Laws are enacted by Congress and signed by the President. They are published in the United States Code (USC). The laws do not have details on implementation.
2. The applicable government agency develops and proposes a regulation. The regulation contains the details on implementation. It is published in the Federal Register and a comment period and hearing is normally held.
3. The Final Rule is published in the Federal Register and the Code of Federal Regulations.

Government Regulations

The two regulations most applicable to chemical plants are:

- Occupational Safety and Health Administration (OSHA):

  29 CFR 1910.119 **"Process Safety Management of Highly Hazardous Chemicals"**

- Environmental Protection Agency (EPA):

  40 CFR Part 68 **"Risk Management Programs"**

OSHA

OSHA: Occupational Safety and Health Administration

Force of law with respect to on-site workplace hazards / accidents. Jurisdiction is only on the plant site, not off-site.

Process Safety / Risk Management

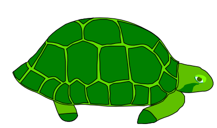
- Management Systems
- Employee Participation
- Process Safety Information
- Process Hazard Analysis
- Operating Procedures
- Training
- Contractor Safety
- Pre-Startup Safety Reviews
- Mechanical Integrity
- Safe Work Practices
- Management of Change
- Emergency Planning and Response
- Incident Investigation
- Compliance Audits

See Table 3-4

EPA

EPA - Environmental Protection Agency

Handles releases outside the plant site.



EPA RMP

Risk Management Plan:

- **Considers offsite impacts due to fires / explosions / toxic release.**
- **Must identify hazards.**
- **Must perform consequence analysis.**

See Table 3-4

Industrial hygiene

Concerns conditions related to workplace injury and sickness
e.g: exposures to toxic vapors, dust, noise, heat, cold, radiation, physical factors, etc.

ANTICIPATION	**Expectation of hazard existence**
IDENTIFICATION	**Presence of workplace exposure**
EVALUATION	**Magnitude of exposure**
CONTROL	**Reduction to acceptable levels**

Chemical plants & labs: requires co-operation from industrial hygiene, safety & plant operations people

Identification

Requires study of

- **CHEMICAL PROCESS**
- **OPERATING CONDITIONS**
- **OPERATING PROCEDURES**

- **Process design**
- **Operating instructions**
- **Safety reviews**
- **Equipment description**
- **Chemical properties MSDS's**

POTENTIAL HAZARDS

- **liquids**
- **vapors**
- **dusts**
- **noise**
- **radiation**
- **temperature**
- **mechanical**

HAZARD DATA

- **physical state / vapor pressure**
- **TLV's**
- **temperature sensitivity**
- **rate and heat of reaction**
- **by-products**
- **reactivity with other chemicals**
- **explosion limits**

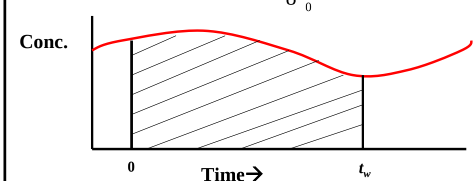
RISK ASSESSMENT: potential for hazard to result in an accident

Evaluating Volatiles

Monitoring air concentrations ⇔ **Variation in time and place**

Time Weighted Average

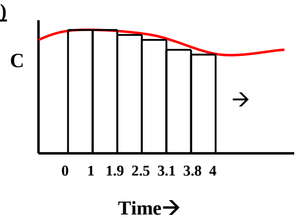
Continuous: $$TWA = \frac{1}{8}\int_0^{t_w} C(t)\,dt$$ **ppm or mg/m³**



Evaluating Volatiles

Intermittent: $$TWA = \frac{1}{8}\sum_1^i C_i T_i$$

Time (hr)	Conc. (ppm)
0	100
1	100
1.9	95
2.5	90
3.1	80
3.8	70



Evaluating Volatiles

Additive effect multiple toxicants: $$\sum_1^i \frac{C_i}{(TLV-TWA)_i} < 1$$

equivalent

Mixture: $$(TLV-TWA)_{mix} = \frac{\sum_1^i C_i}{\sum_1^i \left(\frac{C_i}{TLV-TWA}\right)_i}$$

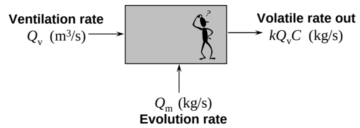
If $\sum C_i < (TLV-TWA)_{mix}$

Then exposure is OK.

Problem: The presence of an additional chemical reduces the exposure concentrations. If you are not aware of the presence of an additional chemical then you might be overexposed when you think you are OK!

Estimating Volatiles

Relevant for design purposes:
- enclosed spaces
- open containers
- filling of vessels
- spill area



Mass Balance: $$\boxed{V\frac{dC}{dt} = Q_m - kQ_vC}$$

Estimating Volatiles

Average conc. steady state $C = Q_m/kQ_v$

More convenient in terms of ppm:

$$C_{ppm} = \frac{V_v}{V_b}\times 10^6 = \left(\frac{m_v/\rho_v}{V_b}\right)\times 10^6$$

$$= \left(\frac{m_v}{V_b}\right)\left(\frac{R_g T}{PM}\right)\times 10^6$$

$$\Rightarrow \quad \boxed{C_{ppm} = \frac{Q_m RT}{kQ_v PM}\times 10^6} \qquad \text{Equation (3-9)}$$

Ideal mixing $k = 1$
Non-ideal $k = 0.1\text{-}0.5$ ⇒ Leads to higher concentrations

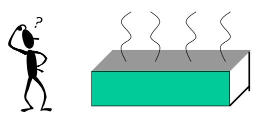
If evolution rate increases or ventilation decrease, concentration will increase.

Example

During a degreasing operation involving trichloroethylene, 10 gallon of TCE evaporates per 8-hour shift.

Data: MW = 131.4, T = 537°R, P = 1 atm

Specific gravity of liquid = 1.46



Ventilation Rate, Q_v = 1000 ft**3/min

Step 1: Determine evaporation rate in lb/min

$$Q_m = \left(\frac{10\text{ gal}}{8\text{ hour}}\right)\left(\frac{1\text{ ft}^3}{7.48\text{ gal}}\right)\left(\frac{62.4\text{ lb}_m}{\text{ft}^3}\right)(1.46)\left(\frac{1\text{ hour}}{60\text{ min}}\right)$$

$$Q_m = 0.254\text{ lb}_m/\text{min}$$

Step 2: Apply Equation (3-9)

$$\boxed{C_{ppm} = \frac{Q_m RT}{kQ_v PM}\times 10^6}$$

$$C_{ppm} = \frac{\left(0.254\frac{\text{lb}_m}{\text{min}}\right)\left(0.7302\frac{\text{ft}^3\text{ atm}}{\text{lb-mole °R}}\right)(537\text{ °R})\text{ x }10^6}{k\left(1000\frac{\text{ft}^3}{\text{min}}\right)(1\text{ atm})\left(131\frac{\text{lb}_m}{\text{lb-mole}}\right)}$$

$$C_{ppm} = \frac{760}{k} \qquad 0.1 \le k \le 0.5$$

$$@\ k = 0.1 \quad C_{ppm} = 7{,}600\text{ ppm}$$

$$@\ k = 0.5 \quad C_{ppm} = 1{,}520\text{ ppm}$$

PEL is 50 ppm, STEL is 200 ppm

What ventilation rate required to reduce below PEL?

Assume k = 0.1 (worst case)

Use Equation 3-9, calculate Q_v

$$50\text{ ppm} = \frac{\left(0.254\frac{\text{lb}_m}{\text{min}}\right)\left(0.7302\frac{\text{ft}^3\text{ atm}}{\text{lb-mole °R}}\right)(537\text{ °R})\text{ x }10^6}{(0.1)(Q_v)(1\text{ atm})\left(131\frac{\text{lb}_m}{\text{lb-mole}}\right)}$$

Q_v = 152,000 ft³/min

Other control methods?

Alternate Control Methods

- Reduce tank surface area, *A*
- Use a hood
- Provide a lid to the container
- Use a different solvent
- Provide personal protective equipment (ppe)
  (Last resort!)

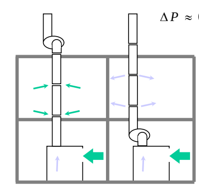
Ventilation

DILUTION Dilution below target concentration
Mixing factor *k* see Table 3-12

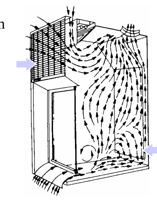
Problems: Requires high air flow and energy costs. Workers always exposed

LOCAL Remove contaminant before exposure workers minimal air flow

$\Delta P \approx 0.01$ atm



Negative Positive
pressure ventilation



- eliminates exposure
- containment device
- shield
- limited workspace

100 ft/min

Bypass laboratory hood

Velometer for Measuring Flow

Hood Operation

← Red liquid level indicates proper hood function.

Evaluating Noise

NOISE PROBLEMS ARE COMMON IN CHEMICAL PLANTS

Relative Noise Intensity $= -10 \log \frac{I}{I_0}$ (dB) $I_0 =$ hearing threshold → (dBA)

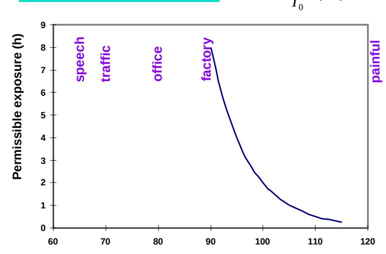


Table 3-8

Similar calculations as volatiles

Exposure to Noise (Table 3-7)

Source	Intensity (dB)
Riveting (painful)	120
Passing Truck	100
Noisy Office	80
Whisper	20

Noise Reduction Ratio (NRR)

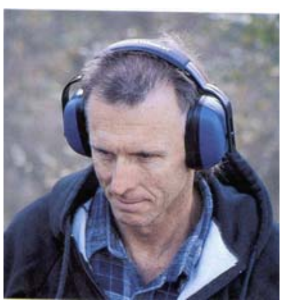
Used for Personal Protective Equipment:

A particular hearing protector has an NRR of 18. If the ambient noise level is 95 dba, what is the worker exposure?

95 dba - 18 dba = 77 dba

Sound Measuring Device→

Hearing Protection



Vaporization

SOURCE TERM:

$$Q_m = \alpha(P^{Sat} - P) = \frac{MKA}{RT_L}(P^{Sat} - P) \approx \frac{MKA}{RT_L}P^{Sat} \qquad \text{(kg/s)}$$

$A =$ area for mass transfer

$$C = \frac{Q_m}{kQ_v} \qquad \text{Eqn. 3-7}$$

Enclosure with $T_L = T$ ➡

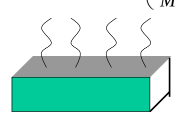
$$C_{ppm} = \frac{KAP^{Sat}}{kQ_v P} \times 10^6 \qquad \text{Eqn. 3-14}$$

Estimating mass transfer coefficient:

$$K = K_0\left(\frac{M_0}{M}\right)^{1/3} \qquad \text{Eqn. 3-18}$$

$K_{water} = 8.3 \times 10^{-3}$ m/s

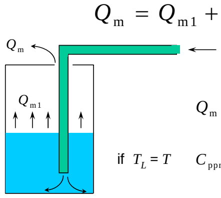
$M = 18$



Filling Vessels

Total Volatiles = Evaporation + Displacement

$$Q_m = Q_{m1} + Q_{m2} \qquad \text{(kg/s)}$$



$$Q_m = (\phi r_f V_c + KA)\frac{MP^{Sat}}{RT_L} \qquad \text{Eq. 3-23}$$

if $T_L = T$ $\quad C_{ppm} = (\phi r_f V_c + KA)\dfrac{P^{Sat}}{kQ_v P} \times 10^6 \qquad \text{Eq. 3-24}$

Splash filling: $\phi = 1$
Subsurface filling: $\phi = 0.5$

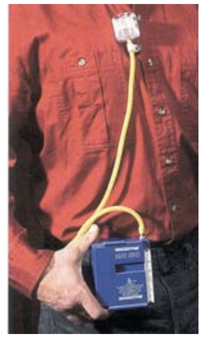
KA often small compared to displacement

Measuring Volatile Concentrations

Colorimetric Tubes

Measuring Volatile Concentrations

Measuring Volatile Concentrations



← Filter unit, usually contains activated charcoal.

This unit goes with the worker and is better at measuring the actual exposure to that person.

← Battery powered air pump.

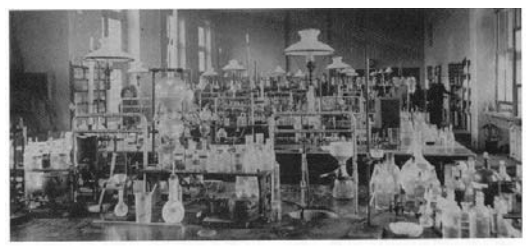
Table 3-9

Control

CHEMICAL PLANT CONTROL TECHNIQUES

Design / Environmental	
Enclosures	**Contain process**
Local ventilation	**Hoods**
Dilution ventilation	**Locker rooms for contaminated clothes**
Wet methods	**Minimize dust by water sprays**
Good housekeeping	**Keep toxics contained**
Personal protection	**Last defense: always compromises workers**

Legacy of the Past!



Legacy of the Past!

Promise of the Present!