Chemical Safety (I)

Chemical Hazards and Controls

Dr Samuel Yu

Health, Safety and Environment Office (HSEO)

HKUST

Important Reminder

Safety training courses provided by HSEO only cover BASIC safety principles. Your supervisor is responsible for your job-specific safety training, including operational safety procedures, departmental safety policies, etc.

Outline Of Presentation

- Local Chemical Regulations
- Evaluation of Chemical Hazards
- Control Approaches
- Description and Control of Different Types of Chemical Hazards
- Local Exhaust Ventilation

Local Regulations

Dangerous Goods Ordinances and Regulations

- Dangerous Goods Ordinance & Regulations Cap295
  - Mainly for fire protection
  - 10 Categories/Classes of DGs
  - Detailed regulations on storage, transport, packaging, segregation of different classes of DGs
  - But not much on usage

New DG Classification Scheme (1)

Class 1	Explosive*
Class 2	Compressed Gases
Class 3	Flammable Liquids
Class 4.1	Flammable Solids
Class 4.2	Substances Liable to Spontaneous Combustion
Class 4.3	Substances Which Become Dangerous in Contact with Water

* Under jurisdiction of Mining, Civil Engineering Dept

New DG Classification Scheme (2)

Class 5.1	Oxidizing Substances
Class 5.2	Organic Peroxides
Class 6.1	Toxic Substances
Class 6.2	Infectious Substances*
Class 7	Radioactive Substances*
Class 8	Corrosives
Class 9	Miscellaneous
Class 9A	Exempted Combustible Goods

* Under jurisdiction of Department of Health

Other Chemical Safety Related Ord & Reg

- Factories & Industrial Undertakings (Dangerous Substances) Regulations Cap59
  - Mainly on labeling requirements
  - Not applicable to universities
- Occupational Safety & Health Ordinance Cap509
  - Applicable to all places of employment
  - “General Duties” clause requires provision of a safe work environment

Evaluation of Chemical Hazards

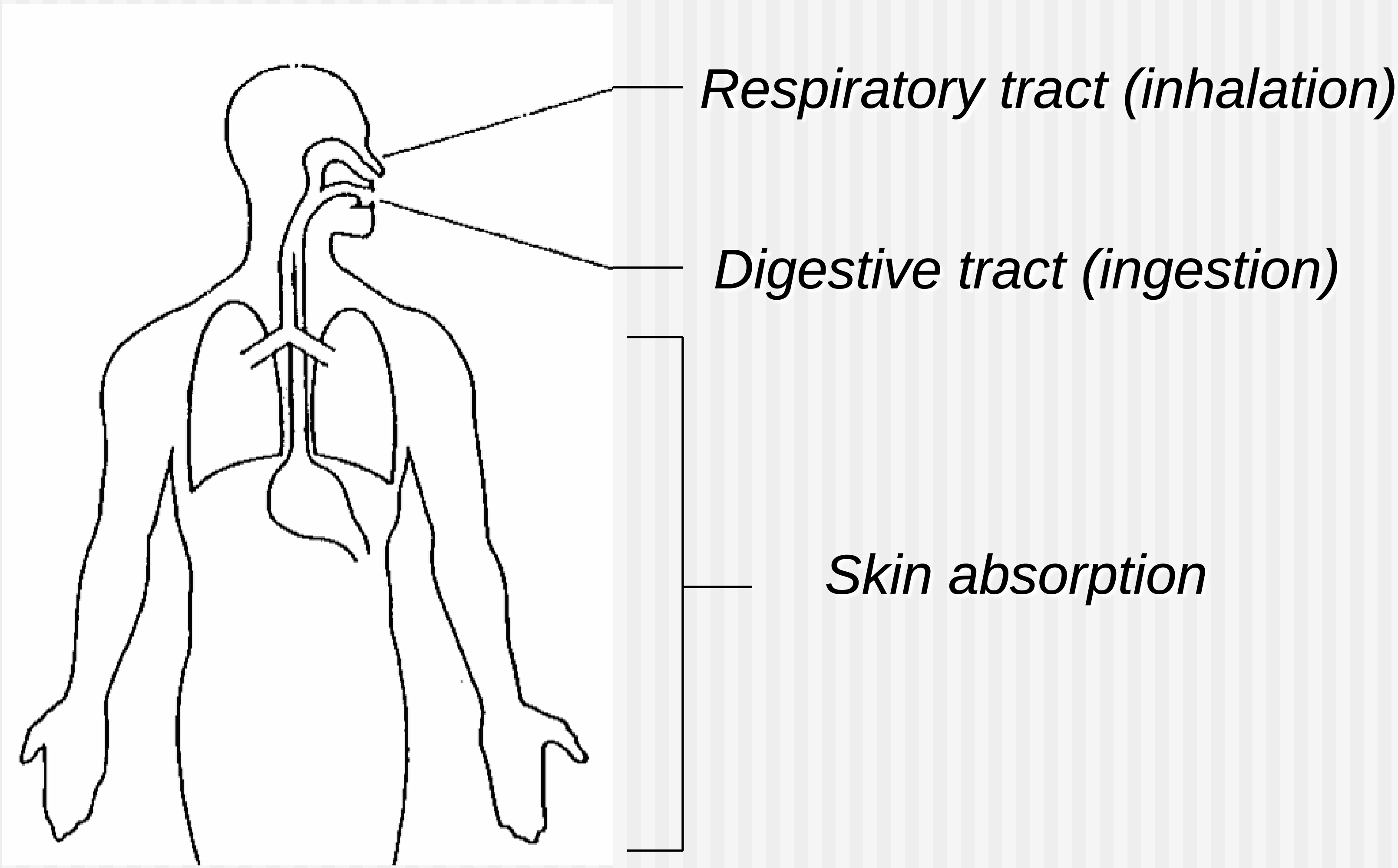
Evaluation of Chemical Hazard

- Toxicity
  - Type of material
  - Physical state
  - Route of entry
- Quantity
  - Nature of operation
  - Duration of operation

Toxicity Depends on Routes of Entry

- Toxicologists refer to “portals of entry”
- Inhalation - Most important industrially
  - Direct access to blood, limited metabolism
  - Potentially serious consequences
- Skin - Most common
  - Dermatitis the most common occupational disease
- Ingestion - Associated with poor personal hygiene or housekeeping

How Chemicals Enter Our Body: Routes of Entry



A Toxicity Reference Scheme

Class	Oral Dose (LD_{50})	For an Average Person
Practically Nontoxic	> 15 g/kg	> 1L
Slightly Toxic	5 - 15 g/kg	0.5 - 1L
Moderately Toxic	0.5 - 5 g/kg	30 - 500mL
Very Toxic	50 - 500 mg/kg	5 - 30mL
Extremely Toxic	5 - 50 mg/kg	7 drops - 5mL
Supertoxic	< 5 mg/kg	A taste (< 7 drops)

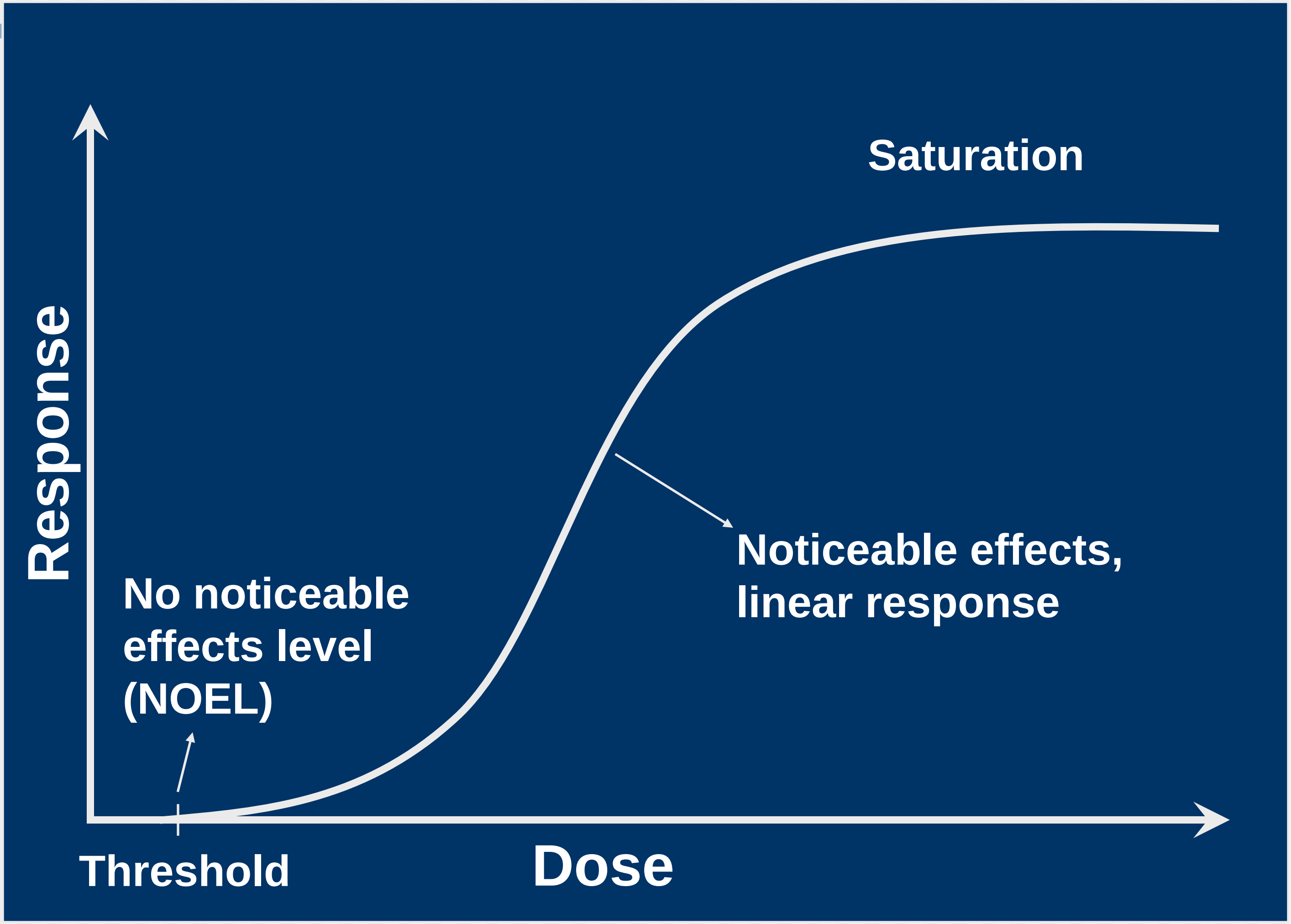
Magnitude of the Hazard Depends on the Dose

- No good or bad chemicals
- All are toxic at some dose
- “The dose makes the poison”

All substances are poisons; there is none which is not a poison. The right dose differentiates a poison and a remedy.

Paracelsus
(1493-1541)

More Dose Means More Risk



Lethal Doses Vary

Material	*rat oral LD_{50} (mg/kg)*
Sucrose	29,700
Vitamin C	11,900
Ethyl alcohol	7,060
Table salt	3,000
Paracetamol	1,944
Metallic arsenic	763
Caffeine	192

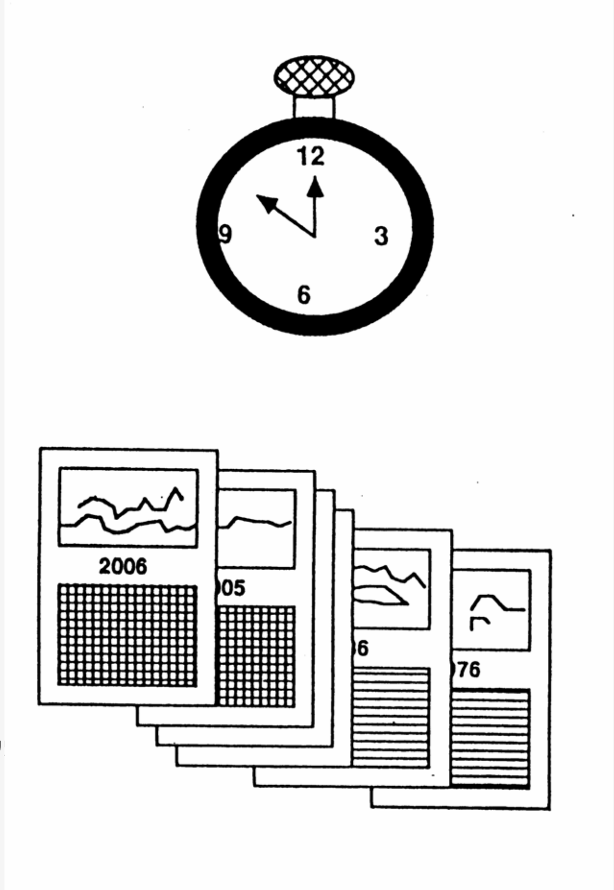
Lethal Doses Vary (Continued)

Material	*rat oral LD_{50}(mg/kg)*
Nicotine	50
Mercury (II) choride	1
Beryllium oxide	0.5
Dioxin (TCDD)	0.02
Botulinum toxin (human)	0.000001

That's a range of 10,000,000,000 = 10^{10}!

Toxics can be grouped by how quickly they act

- Acute toxicity - Fast (seconds - days)
  "You'll know right away!"
  Examples: ammonia, cyanides
- Chronic toxicity - Slow (months - decades)
  "Could catch up with you!"
  Examples: lead, asbestos cadmium

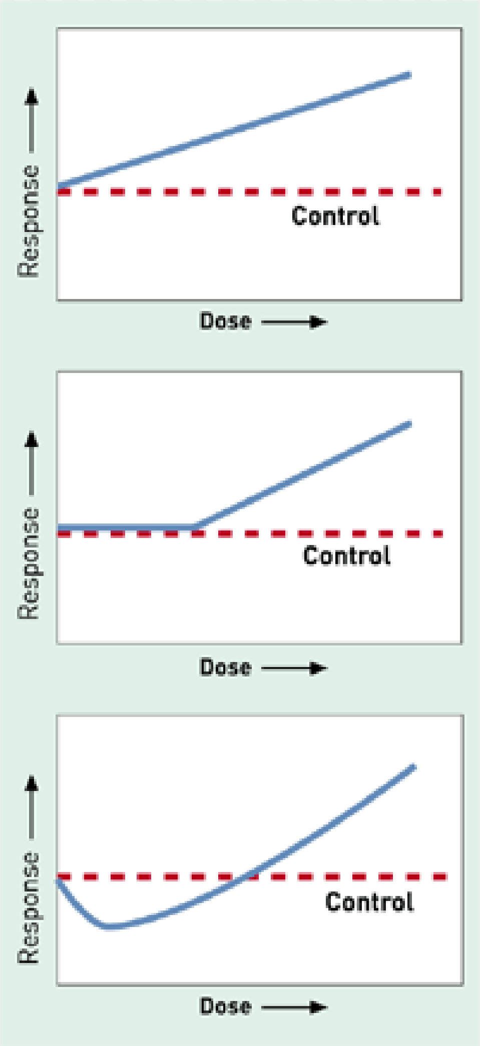


Carcinogens

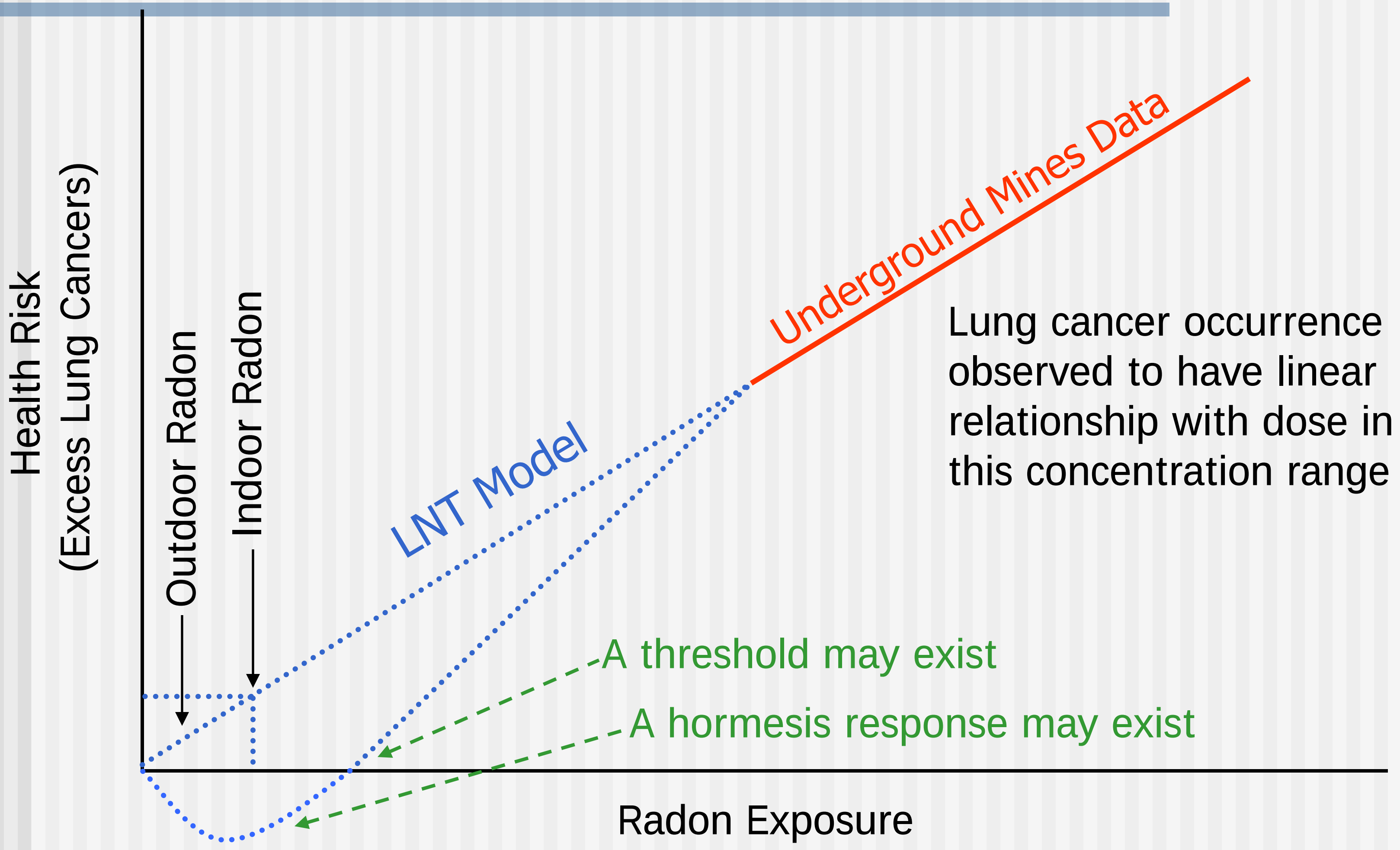
- Carcinogenesis not completely understood
- A multistage process that takes years to occur
- Conservative approach: assume “linear no threshold” dose response
- No “safe level”, only “acceptable risk”

The Problem of Low Dose

- Linear (no threshold)
- Threshold (“safe level”)
- Hormesis (stimulatory effect)



Radon Exposure and Lung Cancer Risk



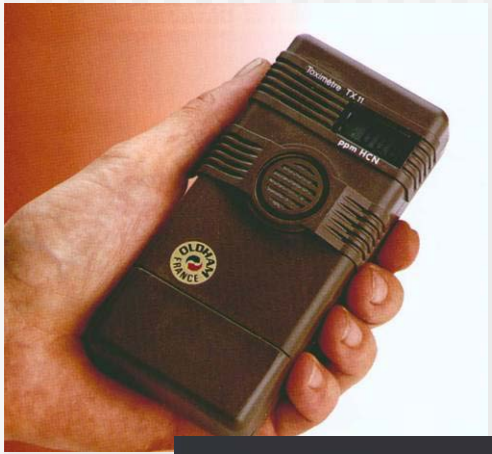
Modified from Dr Edmond T Hui

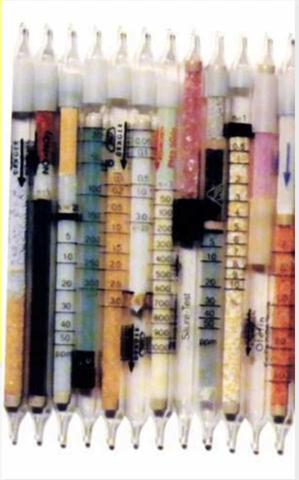
Quantifying Chemical Hazard

- Exposure monitoring
- Airborne chemical concentration
    - Direct measurement
    - Air sampling and laboratory analysis
- Surface chemical sampling
- Bulk sampling and analysis

Monitoring of Airborne Chemical Concentration (1)

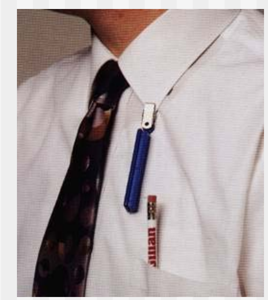
- Direct Measurement
  - On site, real time
  - Electronic instruments, fixed or portable
  - Colorimetric indicator (detector) tubes





Monitoring of Airborne Chemical Concentration (2)

- Sampling and Laboratory Analysis
  - Sampling pumps and various media
  - Air sampling in field
  - Analysis in laboratory



Occupational Exposure Limit - OEL

- Time-Weighted Average (TWA)
  - "the time-weighted average concentration for a conventional 8-hour workday and a 40-hour workweek, to which it is believed that nearly all workers may be repeatedly exposed, day after day, without adverse effect."

American Conference of Governmental Industrial Hygienist (ACGIH) Definition of Threshold Limit Value—Time Weighter Average (TLV-TWA)

Example of TWA Calculation

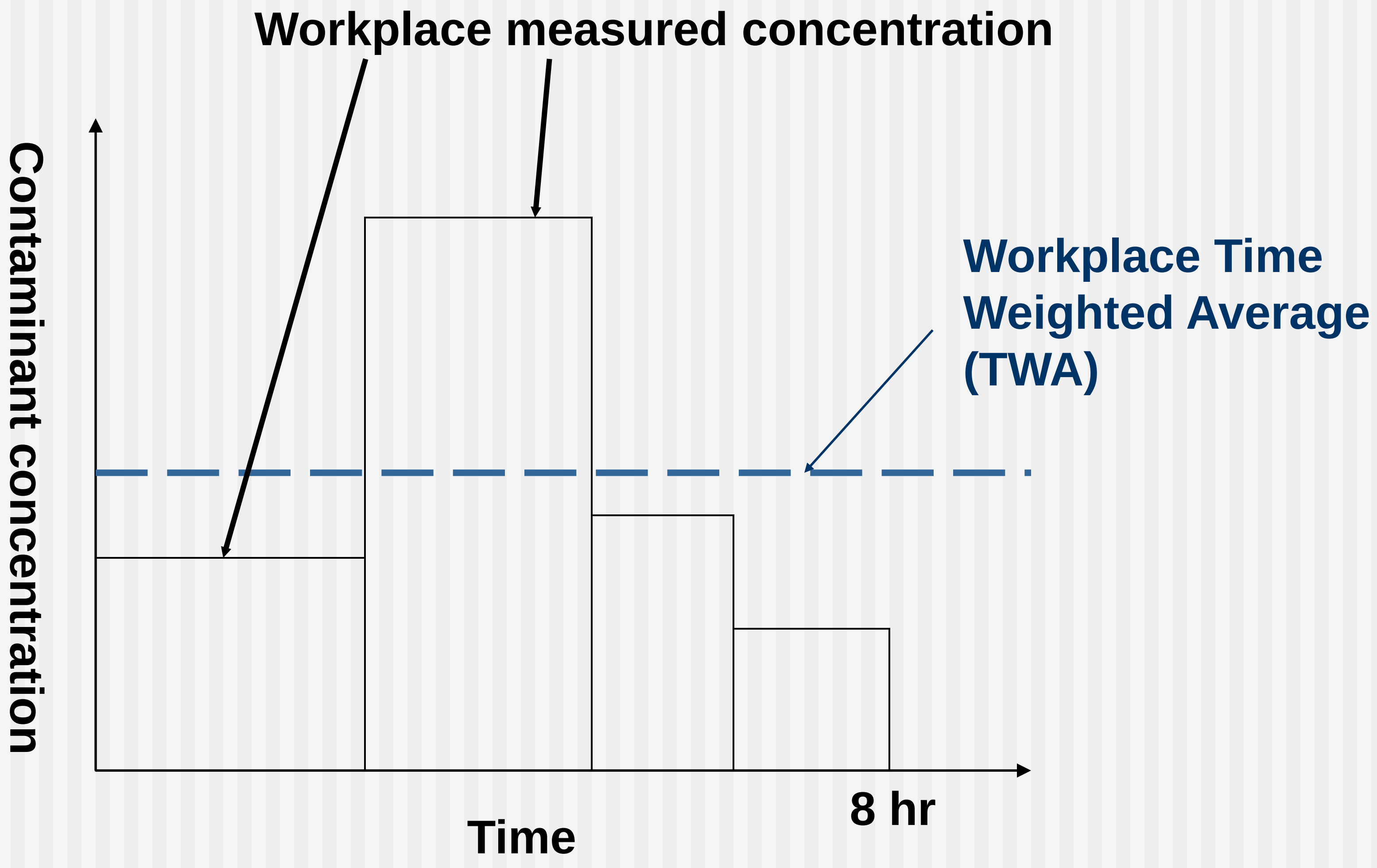
If a worker is exposed to Substance X under the following situation

- 10 units for 1 hour
- 20 units for 1 hour
- 5 units for 6 hours

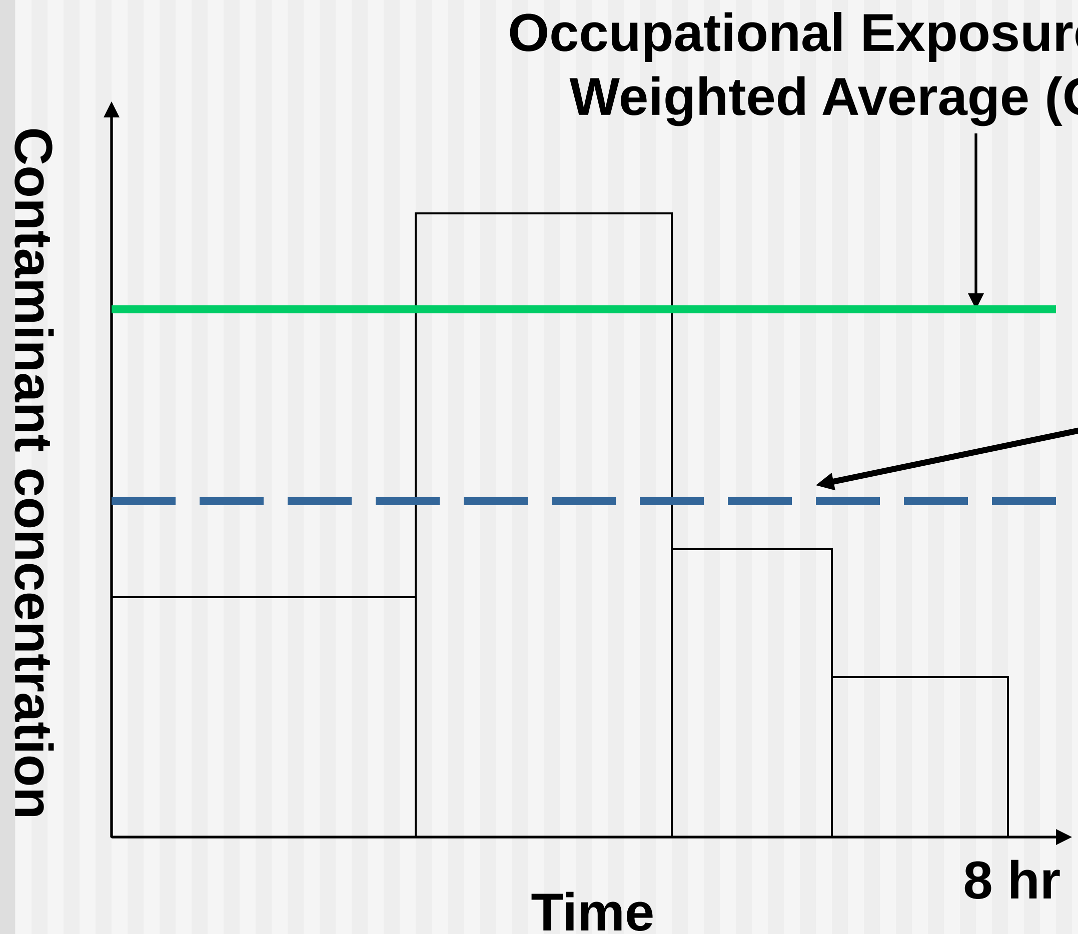
The correct calculation of the TWA is

$[(10 \times 1)+(20 \times 1)+(5 \times 6)] / 8 = 7.5$ units

Workplace Time Weighted Average



Occupational Exposure Limit – Time Weighted Average (OEL-TWA)



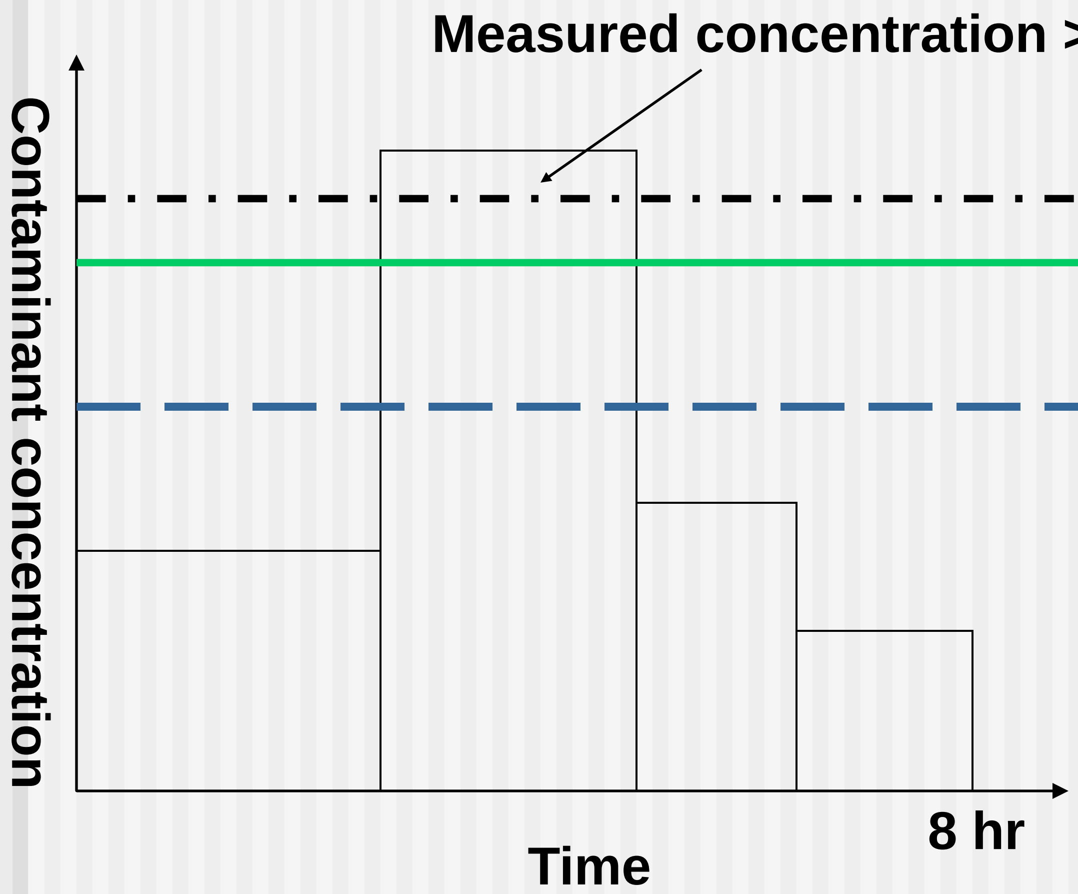
Conclusion:

The workplace TWA is less than OEL – TWA. Therefore, the exposure is acceptable

Occupational Exposure Limit - OEL

- Short Term Exposure Limit (STEL)
  - An STEL is defined as a 15-minute TWA exposure which should not be exceeded at any time during a workday even if the 8-hour TWA is within the TLV-TWA.
  - Exposures above the TLV-TWA up to the STEL should not be longer than 15 minutes and should not occur more than four times per day. There should be at least 60 minutes between successive exposures in this range.

Occupational Exposure Limit – Short Term Exposure Limit (OEL – STEL)

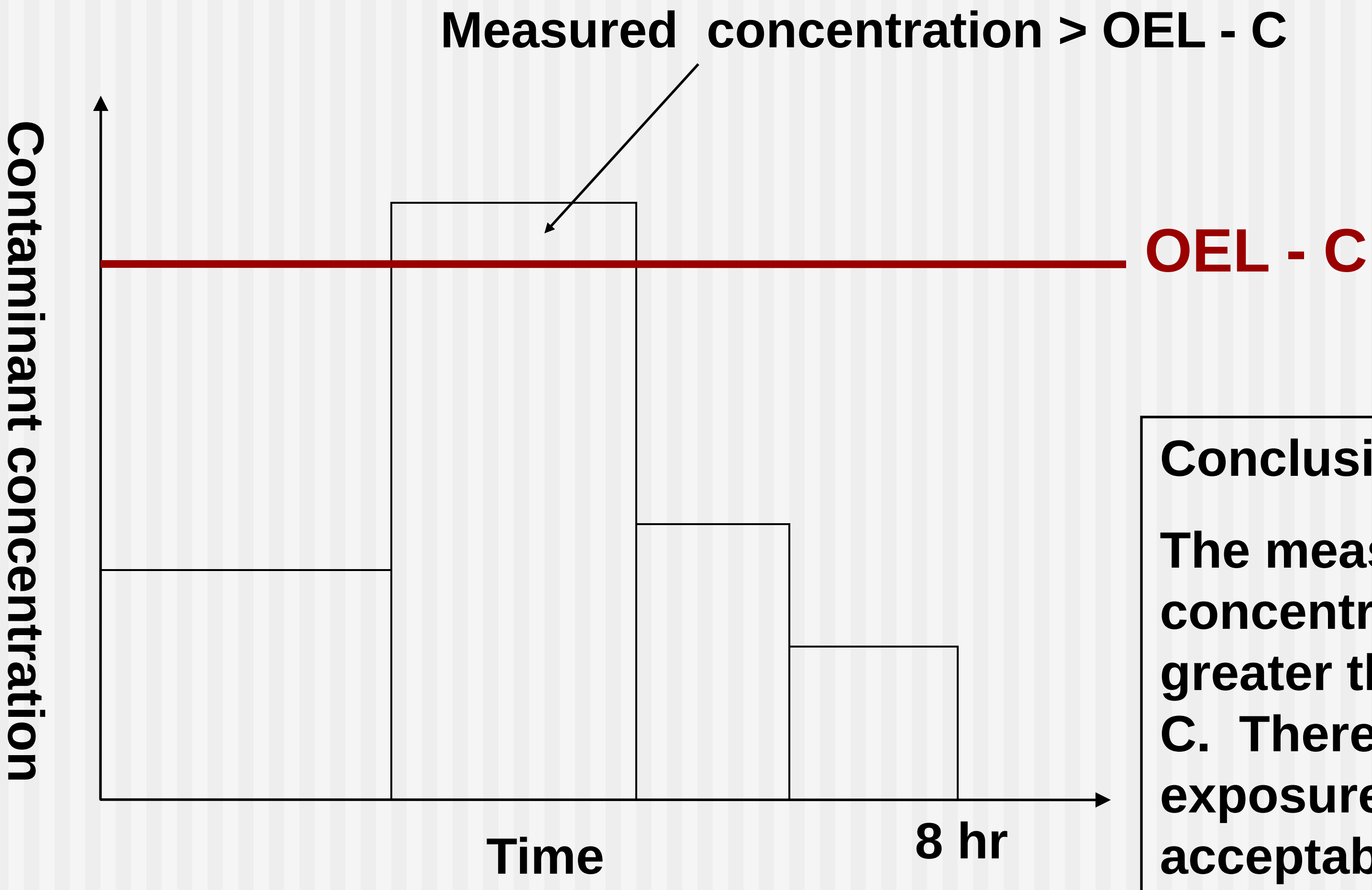


Conclusion:
The workplace TWA is less than OEL-TWA but the measured concentration for one period is greater than OEL-STEL. Therefore, the exposure is not acceptable.

Occupational Exposure Limit - OEL

- Ceiling (C)
  - the concentration that should not be exceeded during any part of the working exposure.

Occupational Exposure Limit – Ceiling (OEL – C)



Conclusion:

The measured concentration is greater than OEL – C. Therefore, the exposure is not acceptable.

Example of Occupational Exposure Limits

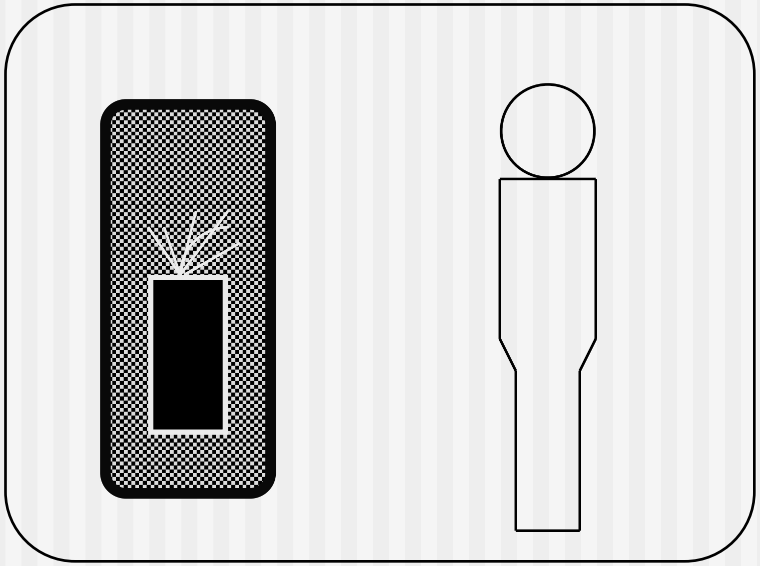
	TWA	*STEL*	*CEILING*
Acetone	500	750	
Benzene	0.5	2.5	
Ethanol	1000		
Hydrogen Cyanide			4.7
Hydrogen Sulfide	10	15	
Nitric Acid	2	4	
Toluene diisocyanate	0.005	0.02	

Units: Parts Per Million volume by volume (ppmv)

Control Approaches for Chemical Hazards

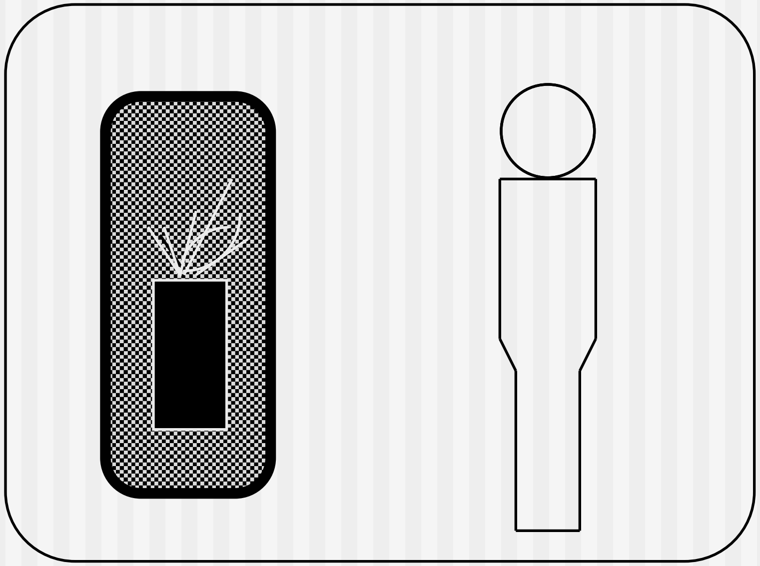
Engineering Controls (I)

- Ventilation
- Isolation / enclosure
- Remote control
- Using less hazardous material
- Interlock
- Built-in safety features



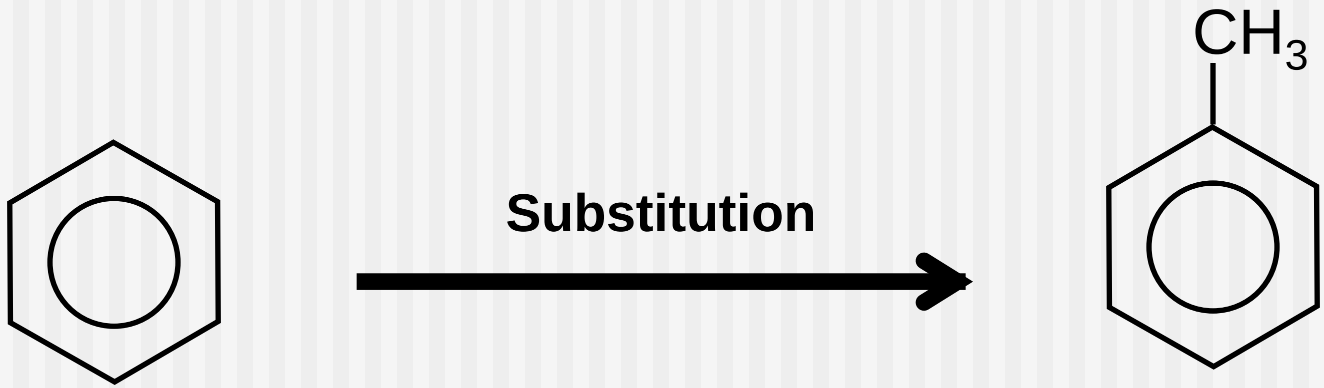
Engineering Controls (II)

- Engineering controls are <u>preferred</u>:
  - “Fool-proof”
  - Easiest to use
  - Best chance of successfully protecting people!



Examples of Engineering Control

Using less hazardous materials



Benzene

Human Carcinogen

Toluene

Harmful

Examples of Engineering Control

Glove Box: Isolation of air and water sensitive chemical

Explosion-proof Refrigerator: Storage of hazardous chemical

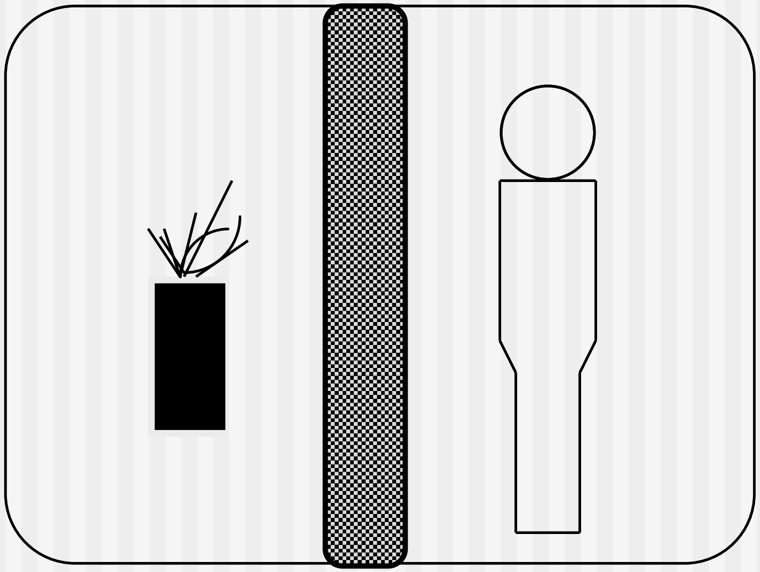
Examples of Engineering Control

Local Exhaust Ventilation

Total Enclosure – Ventilated Cabinet for a fluorine gas cylinder

Administrative Controls

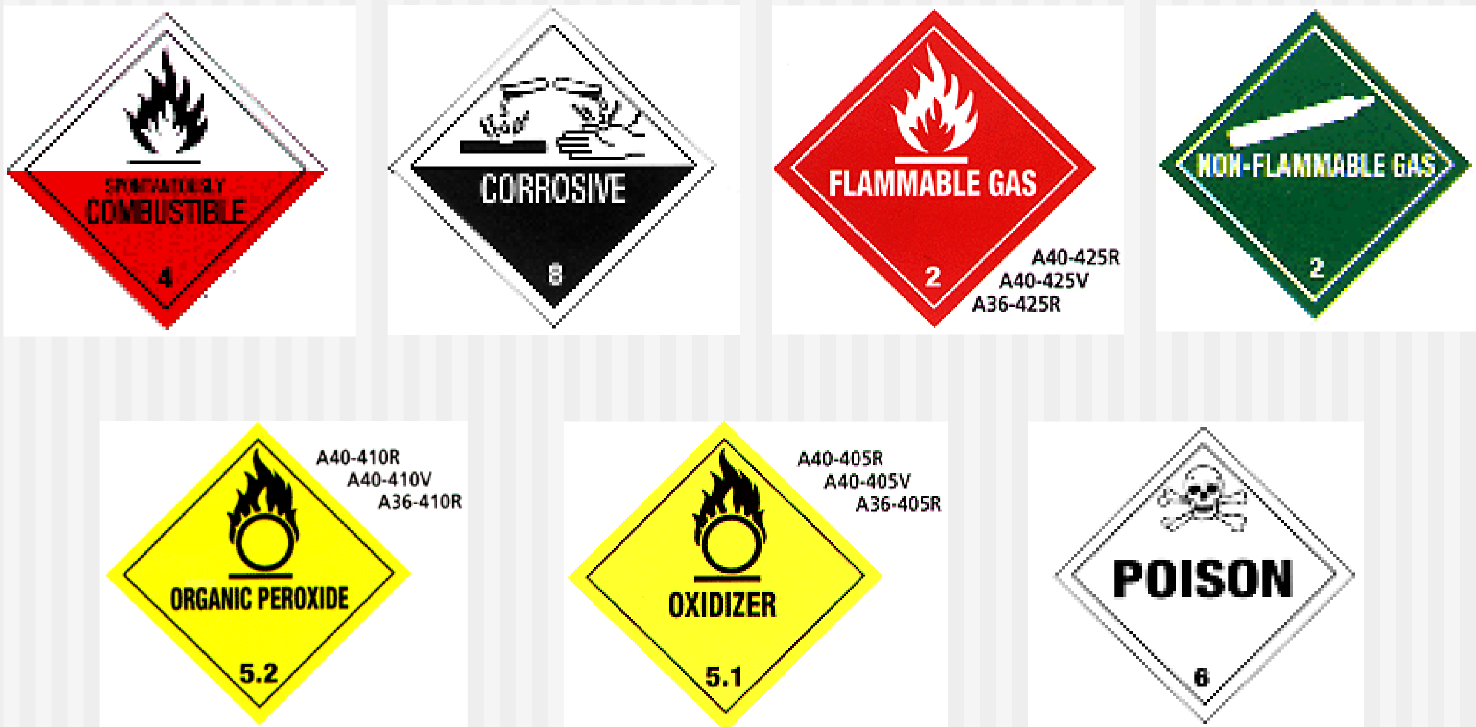
- Work Procedures
- Work shift
- Training
- Warning devices
- Depends on the "human element"
- Less reliable than engineering control



Examples of Administrative Control

Warning Notices

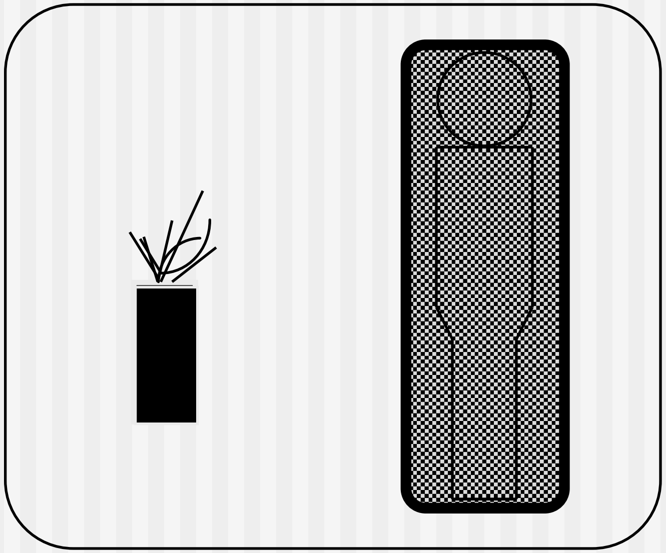
Examples of Administrative Control



Hazardous Warning Labels

Personal Protective Equipment (PPE)

- Last line of defense
- Lowest initial cost
- Depends on "human element"
- Strong demands on supervision
- Need to match PPE & hazards



Examples of PPE

Important Reminder: A Tragedy of PPE Mismatch

- Karen E. Wetterhahn was a professor of chemistry at Dartmouth College
- She became ill and died in 1997, at the age of 48
- A few drops of dimethyl-mercury was accidentally spilled onto her hands protected only by latex glove
- Delayed neurotoxic effects caused her to be hospitalized after 5 months, and she died 10 months after the accident.

Chemical Compatibility of Glove Materials

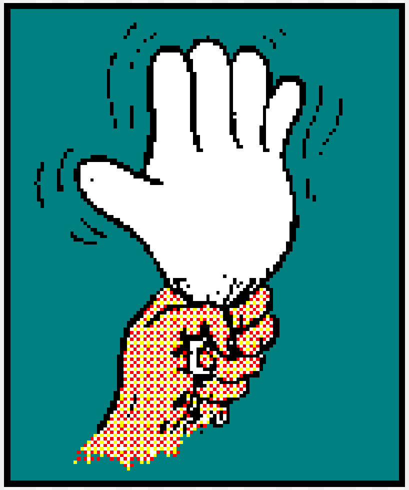
Material	Generally Recommended	Not Recommended
Natural rubber (NR)	alcohols, caustics, ketones, many acids	aromatics, hydrocarbons, many solvents (especially chlorinated or aromatic solvents)
Nitrile Buna Rubber(NBR)	many acids, alcohols, caustics, hydrocarbons	ketones, chlorinated hydrocarbons, strong acids
Neoprene	organic acid, caustics, alcohols, petroleum solvents, ketones	aromatic and chlorinated solvents

Chemical Compatibility of Glove Materials (Continued)

Material	Generally Recommended	Not Recommended
Polyvinyl chloride (PVC)	alcohols, caustics, hydrocarbons	aromatic and chlorinated solvents aldehydes
Butyl rubber	acids, ketones, esters, bases, alcohols, aldehydes	hydrocarbons, halogenated or aromatic hydrocarbons
Viton	chlorinated solvents, aromatics	ketones, ethers, amines, aldehydes
Polyvinyl alcohol (PVA)	solvents, including aromatic, chlorinated & petroleumsolvents	inorganics acids, alcohols, caustics

Reminders for Using Chemical-Resistant Gloves

- Check glove material compatibility with chemicals to be handled, but do not rely on colors
- Check for leak before use
- Dispose worn-out gloves, remember gloves are consumable items, they need to be changed regularly



PPE May Save The Day

Remember the Order of Preference

- Engineering Control
- Administrative Control
- Personal Protective Equipment

Description and Control of Different Types of Chemical Hazards

What Kinds of Chemicals Are We Concerned With? (1)

- Flammables
- Oxidizers
- Peroxidizables
- Shock sensitives
- Pyrophorics
- Water reactives
- Light sensitives

What Kinds of Chemicals Are We Concerned With? (2)

- Corrosives
  - Acids
  - Alkalines
- Toxics
- Asphyxiants
- Cryogens

Precautions Against Highly Reactive Chemicals (I)

- Recognize hazard
- Minimize quantities
- No extraneous materials in area of experiment
- Adequate ventilation for process
- Store properly:
  - Separate from incompatible chemicals
  - Use compatible containers
  - Use spill trays

On-Line Info on Chemical Compatibility

- http://www.ab.ust.hk/sepo/Waste/incomp2.htm
- http://www.ab.ust.hk/sepo/Waste/incomp1.htm
- http://www.ab.ust.hk/sepo/Waste/hwcompe.htm
- http://www.ab.ust.hk/sepo/Waste/hwcompch.htm

Precautions Against Highly Reactive Chemicals (II)

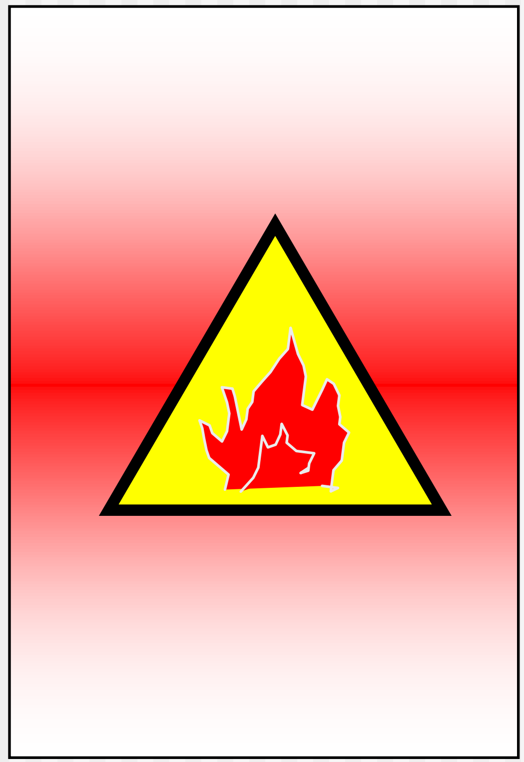
- Put up appropriate barriers if necessary
- Use Personal Protective Equipment:
  - Eye protection (mandatory)
  - Gloves (check compatibility)
  - Clothing (depends on work nature)
  - Respirator (type and cartridge depend on material being handled)
- Proper waste disposal

Flammable Mixtures Only Burn in a Certain Range…

100% vapor:0% air

Too rich

Upper explosive limit

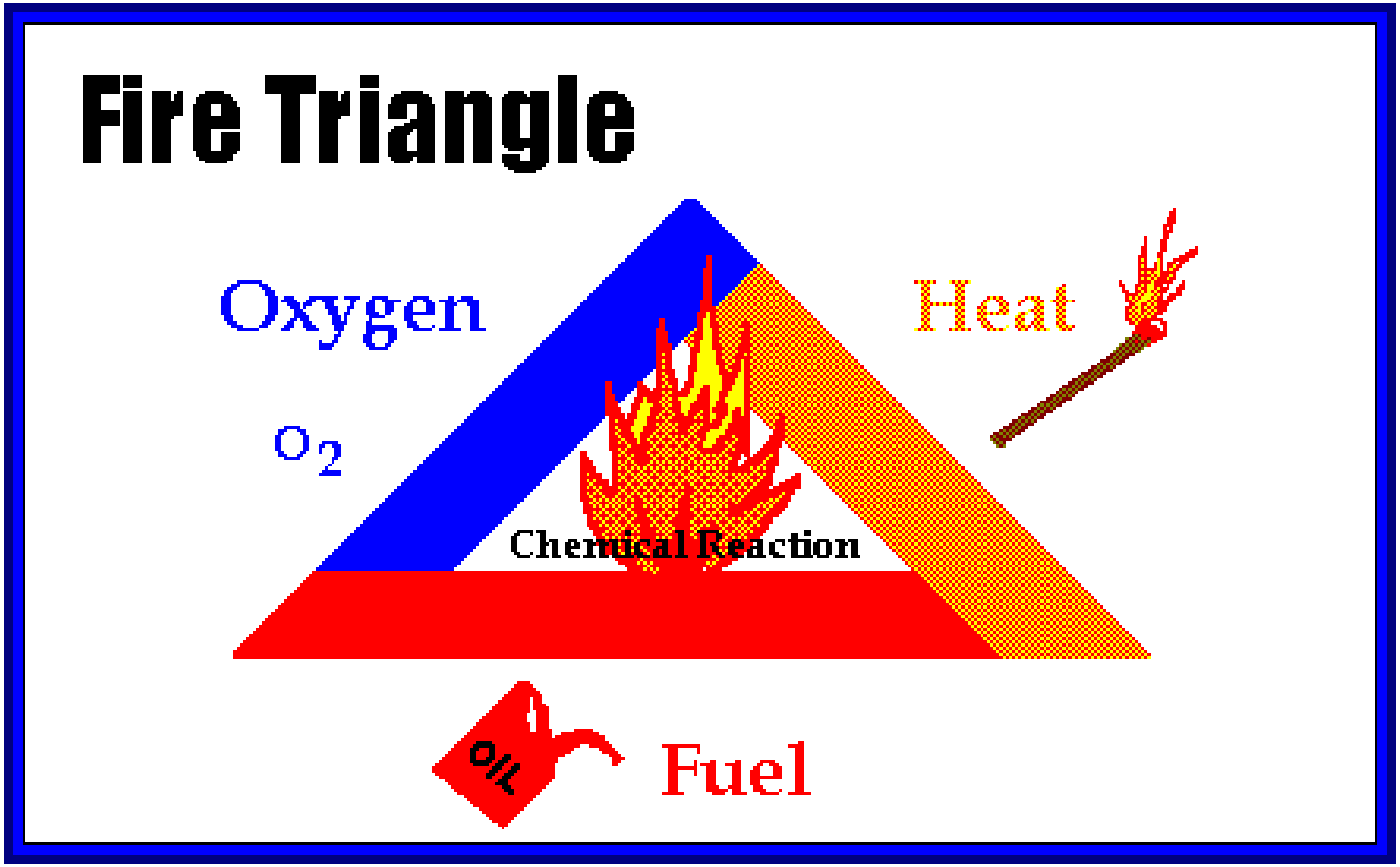


Flammable range

Lower explosive limit

Too lean

0% vapor:100% air


Fire Triangle
Oxygen
O_2
Heat
Chemical Reaction
OIL
Fuel

The Three Elements of Fire

To start a fire, there must be

- Fuel
- Oxygen
- Ignition Source

Therefore, to prevent a fire one needs to prevent the concurrent existence of the three elements

Examples of Common Oxidizers

Gases

Oxygen

Ozone

Halogens (chlorine, fluorine, etc.)

Liquids

Nitric acid

Sulfuric acid

Bromine

Sodium hypochlorite

Solids

Chromates

Bromates

Chlorates

Perchlorates

Nitrates and nitrites

Potassium permanganate

Special Precautions for Oxidizers

- Beware of unexpected reactions
- Store separately from
  - bases
  - reducing agents
  - organic/flammable materials
- Use Corrosion resistant containers

Some Chemicals Can Form Dangerous Peroxides

- Diethyl ether
- Tetrahydrofuran
- Di-isopropyl ether
- Potassium
- Acetaldehyde
- p-Dioxane

Peroxidizable Iso-propanol

Special Precautions for Peroxidizable Materials

- Dating product
  - At time of receipt at Lab
  - At time product is opened
- Test for peroxide every 3 months after opening
- Do not open containers with liquid layers or crystal on cap
- Store properly

A Peroxide Warning Label

WARNING : MAY FORM EXPLOSIVE PEROXIDES

Store in tightly closed original container. Avoid exposure to light, air, and heat. If crystals, discoloration, or layering are visible, contact SEPO immediately. Check for peroxides before distilling or concentrating.

THIS CHEMICAL HAS A LIMITED SHELF LIFE

Received on _______________ Opened on ________________

PEROXIDE TEST RECORD

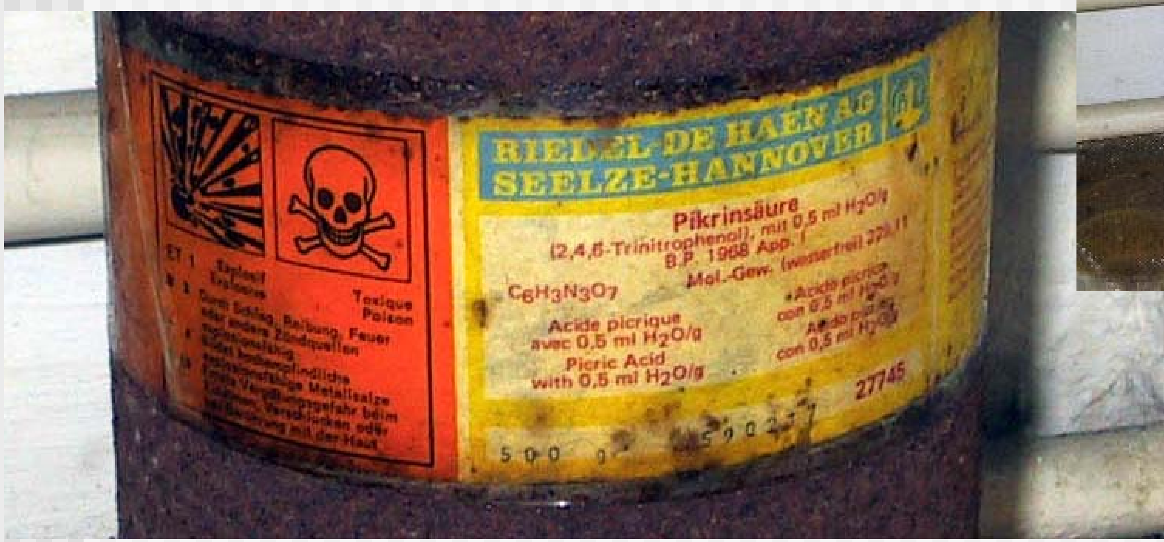
Test Date: ___________ Peroxide:Y/N By: ______________

Retest Date: __________ Peroxide:Y/N By:_______________

Some Chemicals are Shock Sensitive

- Peroxides
- Picric acid
- Azides
- Perchlorates

Anhydrous Picric Acid



Anhydrous Picric Acid is classified as explosive chemical

Protection From Shock Sensitive Chemicals

- Use protective measures against blasting
  - barriers
  - face shields
- Use special procedures
  - perchlorates
  - picric acid

Some Chemicals are Pyrophoric

- Pyrophoric materials are those that are capable of spontaneous combustion in the presence of air
- Common Pyrophoric Compounds
  - Finely divided metals such as Ca
  - Alkali metals such as Na, K
  - White Phosphorous
  - Grignard reagents

Precautions for Pyrophoric Chemicals

- Stored in tightly closed containers under an inert atmosphere (N_2) or liquid (Kerosene)
- Store and handle pyrophoric chemical in a glove box under nitrogen atmosphere

Glove Box Suitable for Handling Pyrophorics

On-Line Info on Explosive or Unstable Chemicals

- Shock Sensitive Chemicals
- Peroxide Chemicals
- Peroxide Tests
- Prolonged Storage of Hazardous Chemicals
- MSDS
- http://www.ab.ust.hk/sepo/chem_info/

Some Chemicals are Water Reactive

Solids	**Liquids**
Alkali metals	Acetyl chloride
Calcium carbide	Chlorosulfonic acid
Magnesium	Silicon tetrachloride
Maleic anhydride	Stannic chloride
Anhydrous aluminum chloride	Sulfur chloride
Phosphorous pentachloride	Sulfuryl chloride
Phosphorous pentasulfide	Thionyl chloride

Special Precautions for Water Reactives

- Minimize scrap production
- Clean scraps up quickly and put in proper containers
- Eliminate ignition sources
- Work in an inert atmosphere
- Proper storage, some may require storage under oil

Corrosives

- Chemicals that attack and damage biological tissues
- Acids
  - inorganic: sulfuric, nitric, hydrochloric
  - organic: formic, acetic
  - hydrofluoric
- Alkalines
  - hydroxides: potassium, sodium, ammonium

Special Precautions for Corrosives

- Avoid contact with skin
- Use proper PPE
  - safety glasses/goggles, face shield
  - corrosive resistant gloves, apron, boots
  - respirator
- Storage in compatible containers
  - formic acid decomposes to CO_2, must use cap with relief device

Toxics

- Include acutely and chronically toxic compounds, mutagens/carcinogens, teratogens
- Focus on chemical hygiene
- Use in fume hood to minimize intake through inhalation
- Follow safety procedures and use suitable PPE to prevent ingestion and skin absorption

Simple Asphyxiants Are Very Common

- Argon, nitrogen, neon, helium, xenon, sulfur hexafluoride carbon dioxide, freons
- Exclude oxygen essential for life
- All could be hazards in confined spaces
  - Small rooms
  - Pits or basements
  - Tanks and Vessels

What Are the Effects of Acute Oxygen Deficiency?

- Shortness of breath
- Headache
- Nausea
- Disoriented/confused
- Muscular weakness
- Uncoordinated
- Distorted vision/hearing
- Unconsciousness/coma/death

How Much Oxygen Do We Need?

Oxygen Conc.	Effects
16%	Feeling dizzy
15%	Lose muscle control
12%	Permanent brain damage
10%	Paralysis can occur
7%	Unconsciousness
6%	Death in 6-8 minutes

Important Note

- These symptoms may not occur.
- A person can slowly, quietly pass out without knowing anything is wrong!!

Protection from Simple Asphyxiants

- Recognize the hazard
- Practice extreme caution in and around CONFINED SPACES:
  - evaluate the workplace
  - use calibrated oxygen monitors
  - be prepared for evacuation
- Proper pressure design/installation
- Handle cylinders and regulators carefully

Chemical Asphyxiant Carbon Monoxide

- It keeps the blood's haemoglobin from carrying oxygen (victims have bright red skin color)
- An odorless, colorless, tasteless gas
  - Occupational Exposure limit 8-hr TWA 25 ppm
  - LC_{lo} (human) 4,000 ppm
  - TC_{lo} (human) 800 ppm
- Also flammable, LEL= 12.5%

Chemical Asphyxiant Hydrogen Cyanide

- It inhibits transfer of oxygen from blood to tissue cells (combines with cell enzymes)
- A slight odor of almond
  - OEL Ceiling 5.7 ppm
  - 270 ppm in air is usually FATAL to humans
- LEL and UEL 6-41%

Precautions for Chemical Asphyxiants (I)

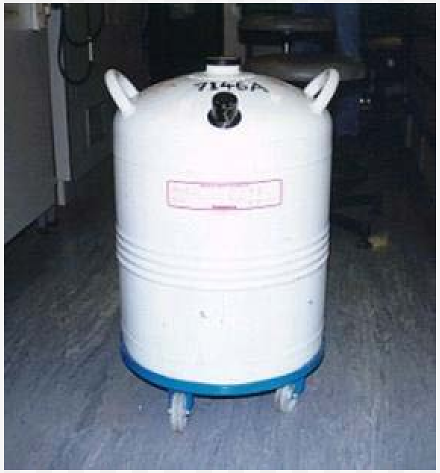
- Avoid accidental formation of gas
  - Beware of incomplete combustion
  - NEVER add acid to cyanide solutions
- Properly design/install gas lines
- Ensure adequate ventilation and exhaust:
  - Laboratory hoods
  - Gas storage cabinets
  - Vented sheds for inactive cylinders

Precautions for Chemical Asphyxiants (II)

- Keep flames, sparks & hot objects away from where gas is in use
- For first aid - speed is essential
  - remove victim from exposure
  - seek immediate medical attention

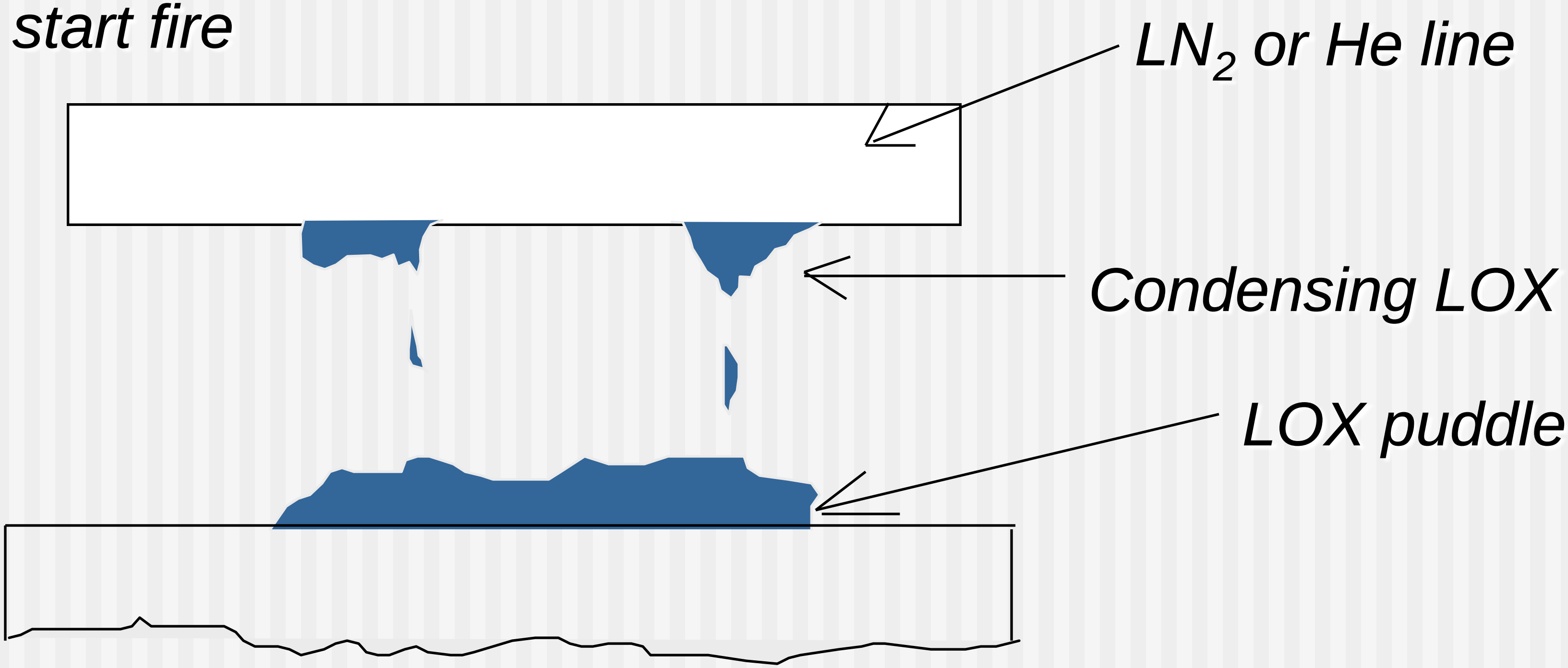
Cryogenic Liquids Can Cause Hazards

- Pressure
- Embrittlement
- Asphyxiation
- Skin burns
- Fire



Watch Out for LOX formation!

- LN_2/LHe are so cold they can condense oxygen out of air
- LOX dripping on asphalt, oils and flammables can start fire



How Do You Protect Yourself From Cryogens?

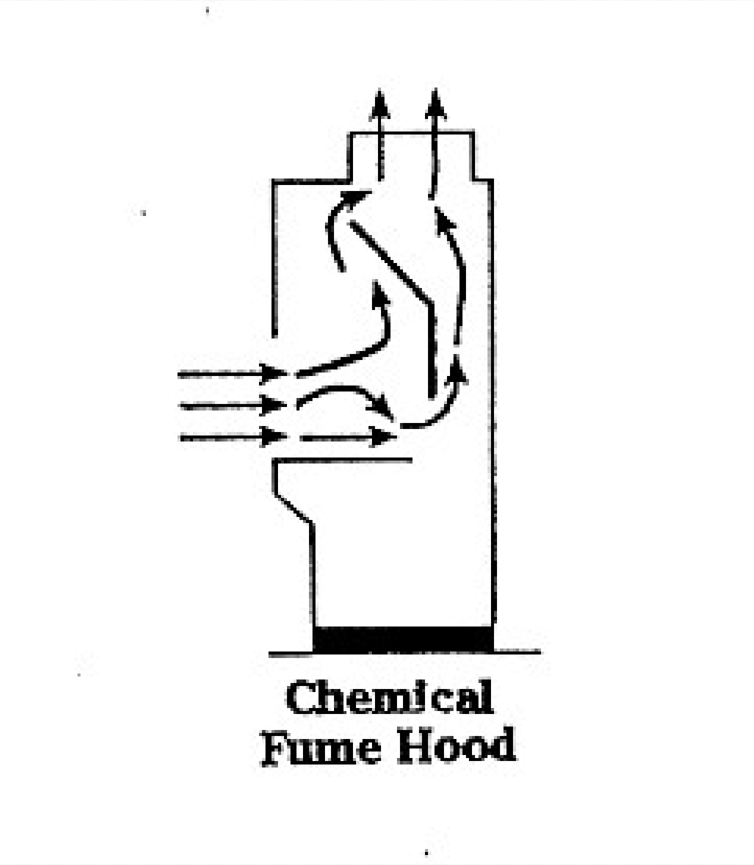
- Clean containers & equipment
- Control the making of mixtures to prevent explosions
- Personal protective equipment:
  - use full face protection
  - wear a lab coat or apron
  - cuffless trousers & high topped shoes
  - gloves which are impervious & large

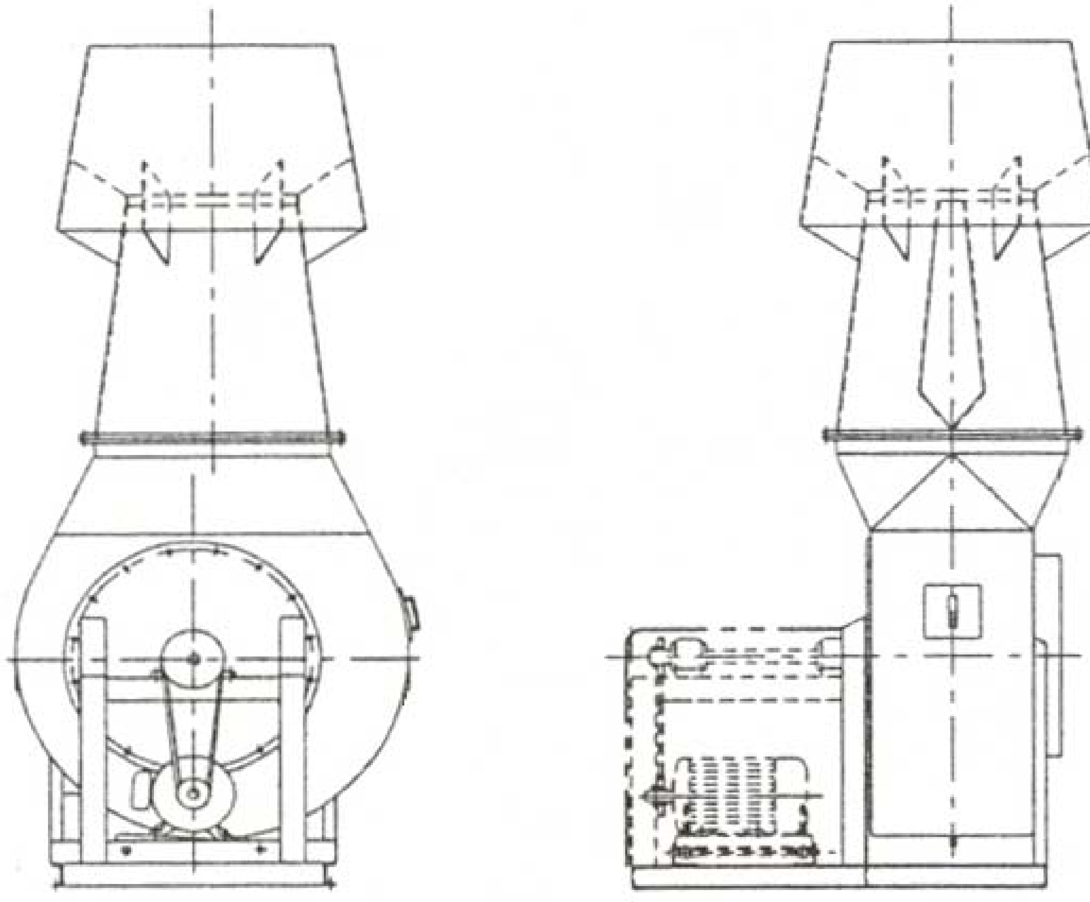
How Do You Protect Yourself From Cryogens?

- Remove watches and rings
- Use Pressure relief devices
- Work in a well-ventilated area

Local Exhaust Ventilation

Chemical Fume Hood





Virtual Stack Fans

Reminder for Fumehood Usage

- Ensure fumehood is running properly, and is regularly maintained
- Always lower sash as much as possible
- Leave at least 15 cm in front and 3 cm at the back of fumehood work area
- If bulky equipment is put inside a fumehood, elevate it to allow air movement
- Maintain good housekeeping, do not use fumehood for storage


NORMAL OPERATING
HEIGHT 500mm
ON
AIR FAIL
AIR SAFE
ALARM
MUTE

What should you do when the low flow alarm is on?

- Stop working in fumehood at once
- Lower sash and wait for alarm to stop
- May mute audible alarm while waiting
- If low flow alarm does not go away after 15 minutes, call FMO Building Services Duty Controller at 6465
- If low flow causes a hazardous situation, call Security Control Centre at 8999

What’s wrong with this fumehood?

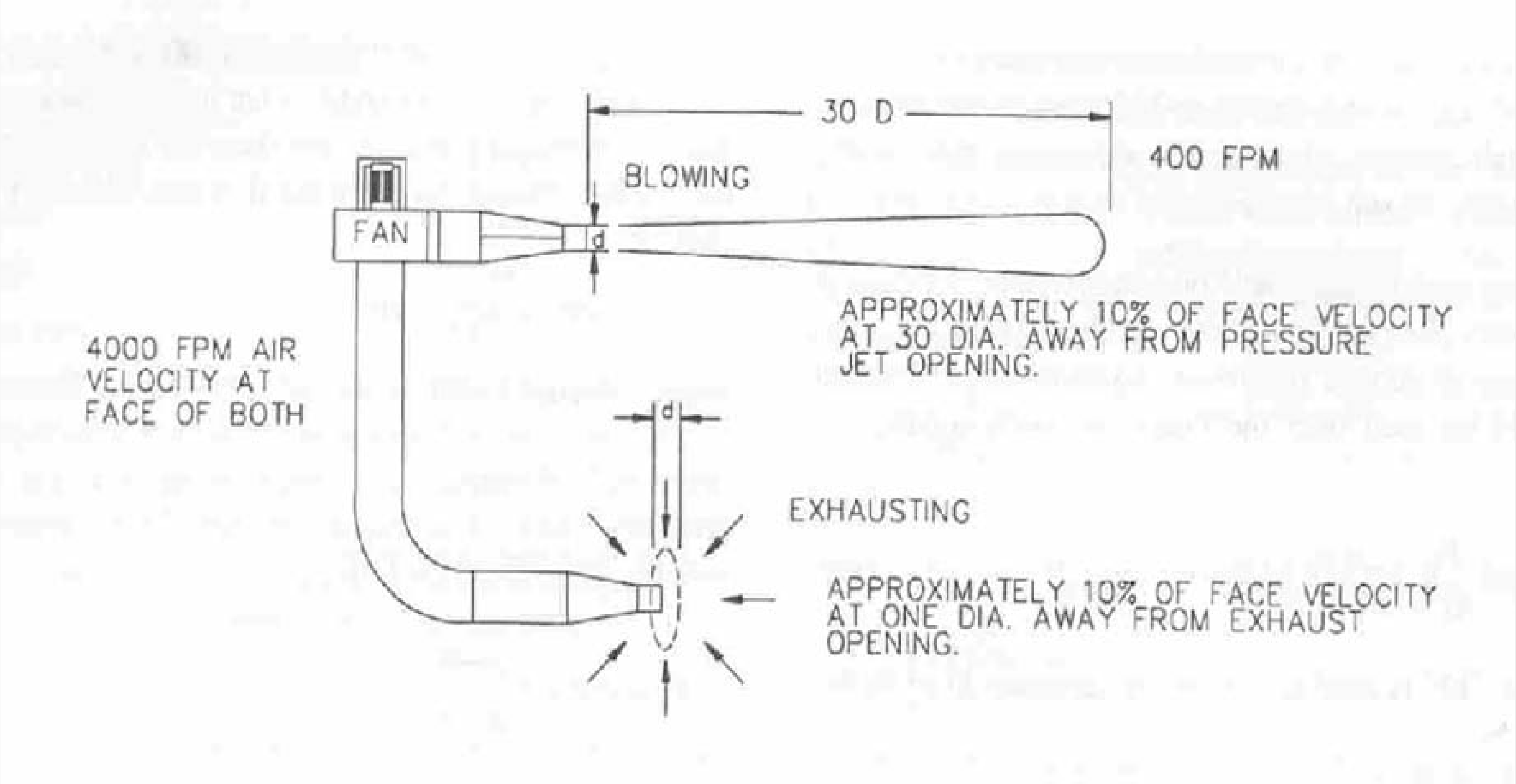
Reminder for Ductless Fumehood Usage

- Ductless fumehoods re-circulate air and rely on filters/treatment systems to remove contaminants, user must ensure filter/system match chemicals to be used
- Check sash position and flow indicator, ensure face velocity is 0.4 - 0.6 m/s
- Look out for saturation alarm or counter reading to check for filter breakthrough
- Never use ductless fumehood for chemical storage

Things to Remember About Local Exhaust Points

- Must have adequate air flow to capture air contaminants
  - Look for label with designed air flow
  - Look for label of field verification of air flow
- The closer the better

Blowing vs Exhausting



~End of Part I~

To be Continued:

Chemical Safety (II) Nanosafety, Waste Management & Emergency Response