Chemical
SAFETY AND SECURITY TRAINING

Chemical Safety and Security Officer Training

Bangkok, Thailand
June 2011

International Year of CHEMISTRY 2011

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Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company,
for the United States Department of Energy's National Nuclear Security Administration
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Sandia National Laboratories

Lab Visit

Lunch

Chemical Toxicology and Physiology

US National Institutes of Health,
National Library of Medicine (NIH/NLM)
on-line
Toxicology Course

I. Basics
II. Toxicokinetics
III. Cellular Toxicology

http://sis.nlm.nih.gov/enviro/toxtutor.html

Simplified Physiology

Major Parts of the Cell

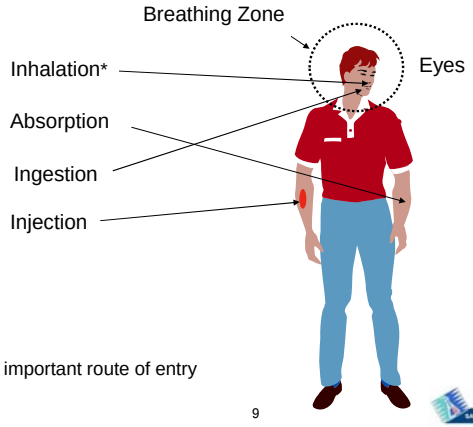
All organisms are made up of cells: (eukaryotic, prokaryotic)

- **Cells membrane** – regulate entry
- **Cytoplasm** – liquid atmosphere of cell
- **Mitochondria** – energy production – ATP
- **Nucleus** – DNA – genes, cell division
- **Golgi** – secretory function
- **Lyzosome** – digestive function

In the Body…

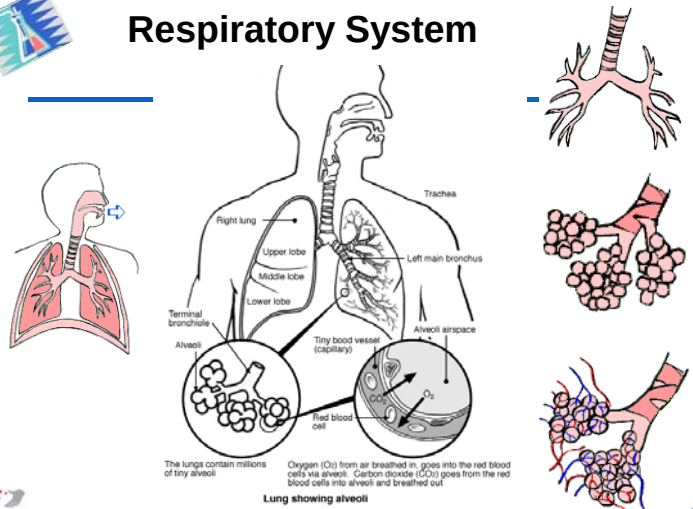
- **Cells** combine to form tissues which are specialized – connective, nerve, muscle
- **Tissues** combine to form organs which can perform complex functions
- **Organs** combine to form systems, e.g., respiratory, reproductive, nervous, circulatory system

Routes of Exposure

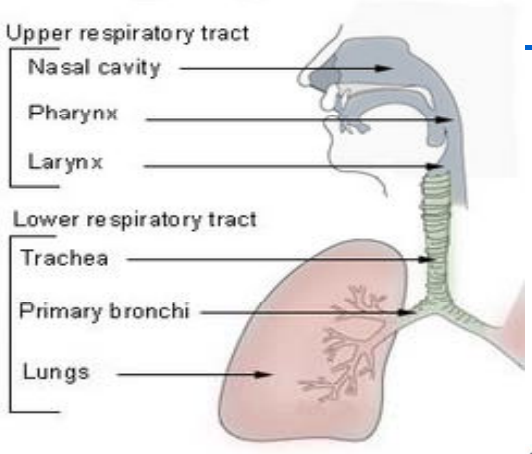


*Most important route of entry

Respiratory System



Conducting Passages



The Lungs
Defense Mechanisms

- **Cilia**
  - Mucus traps dirt and foreign particles.
  - Little hairs (**cilia**) beat back and forth in the airways to move mucus and dirt up where it can be expelled by coughing.
- **Macrophages**
  - Special mobile cells that eat up toxins in the airways and lungs .

- **Requirements:**
  - Regular supply of air with O_2
  - Open, clear airways.

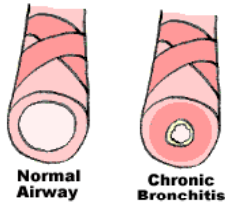
Gas Exchange Region

- About 70 sq meters – the serving area of a tennis court.
- Consists of alveolar duct and alveoli with surfactant to keep open.

- Close contact with capillaries to exchange O_2 for CO_2 and exhale other gases/vapors.

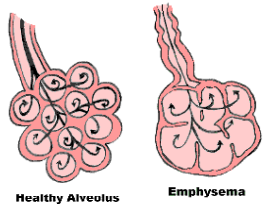
Common Respiratory Issues

Chronic Bronchitis



- Cells inflamed
- Airway narrow and clogged

Emphysema



- Normal elasticity destroyed
- Forcefully blow the air out, pressure on the airways
- Excessive coughing

Routes of Exposure

Inhalation (lungs)

- **Most important route if exposed to gases, vapors, mists, aerosols.**
- **Influenced by respiration rate, concentration, duration.**
- **Key factors for gases and vapors:**
  - solubility and reactivity
- **Key factors for aerosols:**
  - particle size and solubility
    - respirable size: 0.1 μm to 10 μm
  - < 5 μm reach alveolar region

Aerosol Penetration into the Lung

Size (micrometers)	% Deposition
> 20	100% in upper airways
10 – 20	80% upper, 0+ alveoli
5.0 – 10	50% upper, 50% alveoli
0.1 – 5.0	0+ upper, 90+ alveoli

Potential Response

- **Lung tissue damage**
- **Transfer point direct to bloodstream**
  - **transported to target organs - systemic**
- **Responses:**
  - **respiratory tract irritation**
    - **airway constriction**
    - **infection or fluid build-up (edema)**
  - **sensitization**
    - **allergic response, chronic pulmonary disease**
  - **fibrosis**
  - **carcinogenesis**

Certain Effects of Chemicals on the Lungs

- **Irritations** – acid mists (HCl)
- **Edema** – phosgene ($COCl_2$)
- **Emphysema** – smoke (esp. tobacco)
- **Fibrosis** – silicon dioxide (SiO_2)
- **Cancer** – asbestos (mesothelioma)

Asphyxiant / Suffocating Agent

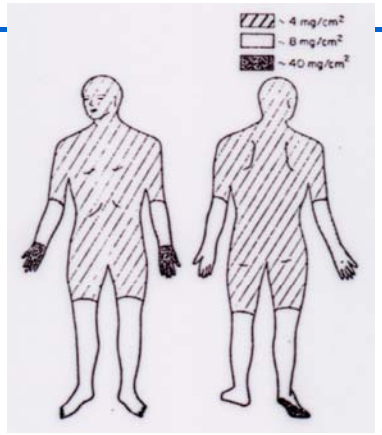
- **Physical** – dilute oxygen in air to below 10%, non-irritant gases – methane, N_2, CO_2, Freon®
- **Chemical** – displace oxygen on hemoglobin – cyanide, carbon monoxide

Routes of Exposure

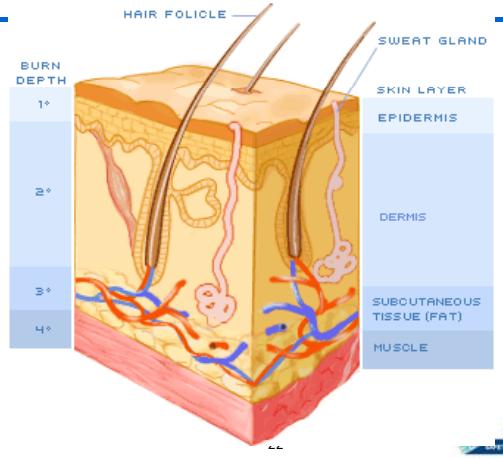
Skin absorption

- **Depends on site of contact**
  - temperature (vasodilatation)
  - thickness, blood flow
- **Depends on skin condition**
  - integrity; pH
- **Time-dependent (duration)**
- **Properties of the toxin**
  - concentration
  - reactivity
  - solubility (in fat/water)
  - molecular size

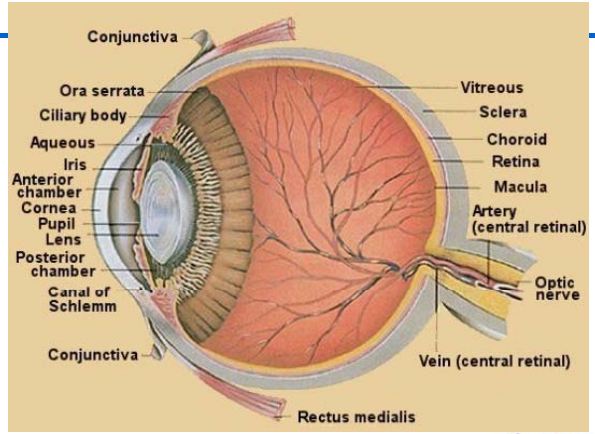
Skin Thickness



Skin



The Eyes



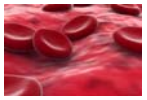
Routes of Exposure

Ingestion (mouth)

- **Rare, but contamination can = intake**
  - mucociliary action of respiratory tract
- **Stomach → GI tract → bloodstream**
- **Absorbed - systemic injury**
- **Liver, kidney; Detoxification process**
  - Inflammation
  - cirrhosis - fibrotic liver disease
  - malignant tumors
- **Factors: physical state, duration**

Routes of Exposure

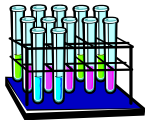
- **Injection**
  - **Directly into bloodstream**
    - "sharps", needles, broken glassware
    - skin puncture or injuries
  - **Bypasses protective mechanisms**
  - **Usually rare in workplace**
    - primarily associated with bloodborne pathogens (biomedical facilitates)
    - especially hazardous in health care industry



Chemical Toxicology

The World of Chemicals

- **Universe of Chemicals > 5 Million**
- **Industrial Inventories ~ 55,000**
- **Regulated Occupationally ~ 600**



Toxicology

Poisons - the adverse effects of substances on living systems.

"All substances are poisons; There is none which is not a poison. The right dose differentiates a poison from a remedy…" – Paracelsus (1493-1541)

Chemical Toxicology – The potential adverse effects and control of chemicals in the workplace.

Terminology

Toxicants	• Substances that produce adverse biological effects of any nature • May be chemical or physical in nature • Effects may be of various types (acute, chronic, etc.)
Toxins	• Specific proteins produced by living organisms (Mushroom toxin or tetanus toxin) • Most exhibit immediate effects
Poisons	Toxicants that cause immediate death or illness when experienced in very small amounts

Basic Concepts

- ***Toxicity*** **– capacity to cause injury**
- ***Hazard*** **– potential harm associated with a specific substance under potential exposure conditions**
- ***Risk*** **– the likelihood or chance that harm will occur under actual conditions**

(Toxicity) X (Exposure) = Risk

Basic Concepts

- **All chemicals have the capacity to be toxic**
- **All chemicals act in the body according to the principles of chemistry, physics and biology**
- **Natural chemicals are not inherently harmless**
- **Synthetic chemicals are not inherently hazardous**

The Dose Makes the Poison

Chemical	Beneficial Dose	Toxic Dose
Aspirin	300-1000 mg	1000-30,000mg
Vitamin A	500 units/d	50,000 units/d
Oxygen	20% in air	50-100% in air

Lethal Dose

Chemical	LD_{50} (mg/kg)
Ethyl Alcohol	7060
Sodium Chloride	3000
Naphthalene	1760
Ferrous Sulfate	1500
Aspirin	1000
Formaldehyde	800
Ammonia	350
Dextromethorphan Hydrobromide	350
Caffeine	192
Phenobarbital	150
Chlorpheniramine Maleate	118
DDT	100
Strychnine Sulfate	2
Nicotine	1
Dioxin	0.0001
Botulinus Toxin	0.00001

There are no harmless substances.

Only harmless ways of *using* substances.

Chemical Toxicology

The study of the effect the chemical has on the body.

Pharmacokinetics

The study of the effect the body has on the chemical.

Toxicity Studies

Determine toxic effect – local effect, target organ, systemic effect, acute, chronic effects.

Determine toxic dose – identify the dose that will produce a given toxic effect.

Factors Influencing Toxicity

- Concentration of toxin
- Duration and frequency of exposure
- Route of exposure
- Environmental factors — temperature, humidity, atmospheric pressure
- Chemical combinations (difficult and expensive to test)

Factors Influencing Toxicity

- Age
- Gender and hormonal status
- Genetic makeup
- State of health—presence of disease or stress
- Nutrition
- Lifestyle

Toxicity Testing Assumptions

- Effects seen in animals apply to humans

- High doses in animals are needed to predict possible hazard to humans

Routes of Chemical Exposure

Occupational

- Inhalation
- Dermal/ocular
- Ingestion

Experimental

- Subcutaneous
- Gavage/ip/iv

Duration of Exposure

- Acute 1 to 5 days
- Subchronic 14 to 90 days
- Chronic 6 months to lifetime

Basic Concepts

- Dose and response can be measured
- Response magnitude is related to dose
- All toxic interactions follow a dose-response relationship

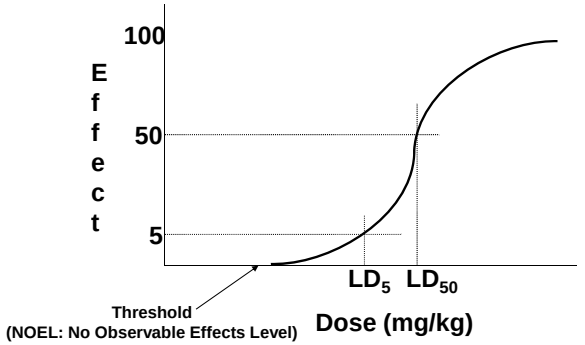
Dose-Response Relationship

- With increasing dose, there is an increase in the number affected and/or an increase in the intensity of the effect: e.g., mortality; cancer; respiratory depression; liver pathology

Dose = (Concentration) x (Time)

Dose-Response Relationship

This relationship is unique for each chemical



Slope of Dose-Response Relationship

- Determines tradeoffs between drug effectiveness and toxicity.
- Low doses may be effective without producing toxicity.
  - More patients may benefit from higher doses.
  - Offset by the higher probability that toxicity or death could occur.
- Slope important in comparing toxicity of various substances.
  - For some, a small increase in dose causes a large increase in response.
  - For others, a much larger increase in dose is required to cause the same increase in response.

Subchronic/Chronic Terms

- NOAEL **no observed adverse effect level**
- LOAEL **lowest observed adverse effect level**
- MTD **maximum tolerated dose**
- RfD **reference dose = safe daily dose for almost every individual**

Threshold Concept

❖ **No-observed (adverse) effect-level (NOEL)(NOAEL)**

– ***the highest dose in an experiment which did not produce an observable effect.***

❖ **Lowest observed (adverse) effect-level (LOEL)(LOAEL)**

– ***the lowest dose which produced an observable adverse effect.***

Dose-Response Relationship

- **Fundamental concept in toxicology**
- **The relationship between the degree of exposure (dose) and the magnitude of the effect (response)**
- **Provides basis for evaluating a chemical's relative toxicity**

Dose and Dosage

- Dose is *quantity* (mg, mL)
- Dosage includes *frequency* (10 mg, 4 times/day)
- Exposure dose – quantity administered
- Absorbed dose – Actual quantity absorbed

Dose-Response Terms

- TD_{lo} – Toxic dose low - lowest dose for effect
- LD_{10} – Lethal dose 10% - dose that causes death in 10% of the test population
- LD_{50} – Lethal dose 50% - dose that causes death in 50% of the test population
- TC_{lo} – Toxic concentration low - used to express toxic concentration *via* inhalation
- LC_{10} – Lethal concentration 10% - dose that causes death in 10% of the test population –*via* inhalation
- LC_{50} – Lethal concentration 50% - concentration that causes death in 50% of the test population *via* inhalation

Concentration Units

Mass per Volume

- mg/m^3 (milligrams per cubic meter)
- $\mu g/m^3$ (micrograms per cubic meter)
- ng/m^3 (nanograms per cubic meter)
- PPM: Parts of a substance per million parts of air
  - 1 minute in 2 years
- PPB: Parts of a substance per billion parts of air
  - 1 second in 32 years
- PPT: Parts of a substance per trillion parts of air
  - 1 second in 320 centuries (1 century = 100 years)

Unit	Gram Equivalent	Exp. Form
Kilogram (kg)	1000.0 g	10^3 g
Gram (g)	1.0 g	1 g
Milligram (mg)	0.001 g	10^{-3} g
Microgram (µg)	0.000,001 g	10^{-6} g
Nanogram (ng)	0.000,000,001 g	10^{-9} g
Picogram (pg)	0.000,000,000,001 g	10^{-12} g
Femtogram (fg)	0.000,000,000,000,001 g	10^{-15} g
Attogram (ag)	0.000,000,000,000,000,001 g	10^{-18} g
Zeptogram (zg)	0.000,000,000,000,000,000,001 g	10^{-21} g

Dose Units

Mass per weight or surface area of subject:

- **Quantity per unit mass (mg/kg)**
- **Quantity per unit area of skin surface (mg/m^2)**

Pharmacokinetics

Rate of:

- **Absorption (uptake) – chemical enters**
- **Distribution (transportation) – spread/storage**
- **Metabolism (biotransformation) – processing**
- **Excretion – elimination**

Metabolism

One purpose of metabolism is to make the chemical more water soluble so it can be excreted.

Done by adding oxygen molecules in the form of -OH, =O, -COOH, or by conjugation with glutathione, sulfonate, glycine, etc.

Some chemicals are not directly carcinogenic, but are metabolized to intermediates, e.g, epoxides, which are highly carcinogenic.

Metabolism, cont'd.

Chemicals not metabolized are stored in the body (e.g.):

- **Lipid soluble materials in fat cells**
- **Metals are bound to proteins (hemosiderin)**
- **Dusts are deposited at surface of lung**

This is why tattoos stay in place!

Metabolites

Benzene (C_6H_6)
carcinogenic
phenol, S-phenylmercapturic acid in urine

Toluene

CNS depressant
hippuric acid in urine

Ethyl benzene

irritant, dermatitis
mandelic acid in urine

Xylene ($C_6H_4(CH_3)_2$)
CNS, irritant
methyl hippuric acid in urine

Styrene

dermatitis
mandelic acid in urine

Interaction of Chemicals

- **Additive Effect**
  - **Combined effect of 2 chemicals equals sum of each agent alone…(2 + 3 = 5)**
- **Synergistic Effect**
  - **Combined effect of 2 chemicals is greater than sum of each agent alone…(2 + 3 = 20)**

Interaction of Chemicals

- **Potentiation**
  - **One substance does not have toxic effect on certain organ or system, but when added to another chemical, it makes the latter more toxic…(0 + 2 = 10)**
- **Antagonism**
  - **2 chemicals, when given together, interfere with each other's actions or one interferes with the action of the other chemical…(4 + 6 = 8)**

Site of Effects

- **Local**
  - **Effects occurring at site of first contact between biologic system and toxicant**
    - **Ingestion of caustic substances**
    - **Inhalation of irritant materials**
- **Systemic**
  - **Require absorption and distribution of toxicant to a site distant from entry point where effects are produced; most substances produce systemic effects**
    - **CCl_4 effects on the liver**

Target Organs for Chemicals

Systemic toxin - affects entire body or many organs rather than a specific site, e.g., KCN affects virtually every cell and organ in the body by interfering with the cell's ability to utilize oxygen.

Toxicants - may also affect only specific tissues or organs while not producing damage to the body as a whole. These specific sites are known as Target Organs.

Benzene - a specific organ toxicant that it is primarily toxic to the blood-forming tissues.

Lead - has three target organs (central nervous system, kidney, and hematopoietic system).

Comparative Toxicity

Toxicity Rating	Dose for a 70 kg Person (154 lb)	
Super Toxic	< 5 mg/kg	(a taste, < 7drops)
Extremely Toxic	5-50 mg/kg	(7 drops – 1 tsp)
Very Toxic	50-500 mg/kg	(1tsp – 30g)
Moderately Toxic	0.5-5 g/kg	(30g – 500g)
Slightly Toxic	5-15 g/kg	(500g – 1kg)
Practically Nontoxic	> 15 g/kg	(>1kg)

Target Organs

Organs selectively affected by harmful agent:

- Lungs (pneumotoxicity)
- Blood (hematotoxicity)
- Liver (hepatotoxicity)
- Kidneys (nephrotoxicity)
- Nervous system (neurotoxicity)
- Immune system (immunotoxicity)
- Embryos/fetuses (reproductive & developmental toxicity)

Target Organ Effects

Toxins	Target organ	Signs & Symptoms	Examples
HEPATOTOXIN	LIVER	JAUNDICE	CCl_4
NEPHROTOXINS	KIDNEY	EDEMA	HALOGENATED HYDROCARBONS
NEUROTOXINS	CNS	NARCOSIS BEHAVIOR	MERCURY
HEMATOPOIETIC SYSTEM	HEMOGLOBIN	CYANOSIS	CO, CS_2
LUNG AGENTS	PULMONARY TISSUE	COUGH,CHEST TIGHTNESS	SILICA, ASBESTOS
REPRODUCTION TOXIN	REPRODUCTIVE SYSTEM	BIRTH DEFECTS	LEAD
CUTANEOUS AGENTS	SKIN	RASHES; IRRITATION	KETONE
EYE HAZARDS	EYES	CONJUCTIVITIS	ORGANIC SOLVENTS

Target Organs

Liver Diseases

- Fatty liver – carbon tetrachloride
- Cirrhosis – ethanol
- Liver cancer – vinyl chloride and chlorinated solvents/pesticides

Target Organs

Skin

The protective barrier wrapped around the body (surface area about 2 m^2).

Helps maintain temperature, prevents water soluble materials entry, site of excretion, sensory activities, protective coating.

Target Organs

Sensory Activities

- Heat, touch, and pain receptors
- Irritation/corrosion
- Sensitization/allergy (immune system)
- Phototoxicity (light directly, sun burn)
- Photoallergy (light + chemical)

Target Organs

Skin Diseases

- Sensitization – chemical allergy
  - TDI – toluene – 2,4-diisocyanate
- Oil/coal tar acne – chloroacne
  - PCBs-polychlorinatedbiphenyls
- Contact dermatitis – fat soluble solvents
- Leukoderma (depigmentation) – H_2O_2
- Allopecia (loss of hair) - thallium

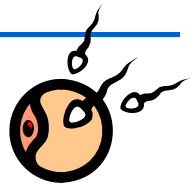
Target Organs

Reproductive and Developmental Disorders

Concern for spermatogenesis, hormonal status, maternal toxicity, and embryo or fetal toxicity.

Target Organs

Spermatogenesis



- **Rarely destroys the testes.**
- **Usually blocks sperm development.**
- **EGME (ethylene glycol monoethyl ether)**
- **Completely reversible after exposure ends.**

Target Organs

Developmental Effects:

- **Lethality – resorptions/stillbirths**
- **Toxicity – body weight/behavioral effects**
- **Teratogenicity – malformations (thalidomide)**
- **Delayed development/structural anomalies/variations**

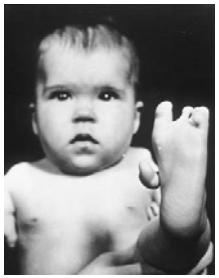
Target Organs

Teratogenicity

A specific type of developmental toxicity

Derived from Greek - monster formation

e.g., thalidomide



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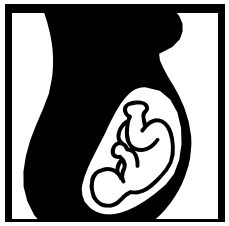
Target Organs

Maternal Toxicity:



- Oxygen depletion
- Nutrient intake
- Lead or other metals

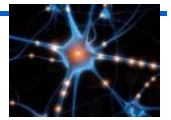
Target Organs

Maternal Toxicity:

- The ovary is more protected than the testes. So, it is not toxicity, but changes in hormonal regulation that is upset
- Endocrine modulation, DDT, and raptor eggs, ovulation, gestation

Target Organs

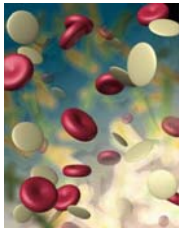
Nervous System:



- CNS depression – many organic solvents
- Cholinesterase inhibition – organophosphorus & carbamate pesticides
- Nerve conduction velocity – myelin sheath, peripheral nerve destruction – n–hexane

Target Organs

Circulatory System:



- Hemoglobin – CN and CO
- Red cells – lysis or lead poisoning
- Leukemia – benzene
- Arterial blockage – cholesterol, HDL/LDL

Toxic Effects of

Some Specific Chemicals

Metals

Arsenic (in detail)

A. Exists in elemental form and in the tri- and pentavalent oxidation states, copper mining & smelting

B. Toxicity rating: RAs –X < As^{+5} < As^{+3} < AsH_3

C. Absorption, distribution and excretion

1. Variable absorption, soluble salts well absorbed and insoluble salts are poorly absorbed
2. Distribution: liver and kidney, hair and nails
3. Excretion
   - **a) Excreted in urine**
   - **b) Half-life about 2 days**

D. Biochemical mechanism of toxicity

1. As^{+5} reacts with thiols, uncouples energy production
2. As^{+3} uncouples oxidative phosphorylation

Arsenic (detail continued)

E. Arsenic poisoning

1. Early signs and symptoms
   - **a) Diarrhea**
   - **b) Skin pigmentation**
   - **c) Hyperkeratosis**
   - **d) Edema of lower eyelids, face and ankles**
   - **e) Garlic odor of breath**
2. Progression
   - **a) Dermatitis and keratosis of palms, soles – skin cancer**
   - **b) Enlarged liver**
   - **c) Renal injury**
   - **d) Peripheral neuropathy (legs more than arms – contrast to lead)**
   - **e) Encephalopathy**
   - **f) Aplastic anemia, lung & skin cancer**

F. Arsine (AsH_3)

1. Gas
2. Hemolysis

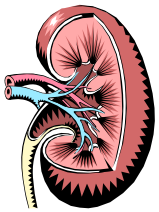
Cadmium (summary)

A. Acute cadmium poisoning

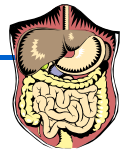
1. Oral – GI effects
2. Inhalation – local irritation of respiratory tract

B. Chronic cadmium poisoning

1. Kidney - **Most cadmium sensitive organ**
2. Lungs
   a) **After inhalation**
   b) **Emphysema**
3. Cardiovascular – hypertension
4. Bone
5. Testes – sensitive after acute, not after chronic
6. Itai-itai (ouch-ouch disease)



Lead (Summary)



A. Acute lead poisoning

1. **Rare**

B. Chronic inorganic lead poisoning (plumbism)

1. **Gastrointestinal effects**
   a) **More common among adults**
   b) **Referred to as lead colic, often symptoms for which patient seeks relief**

C. Organic lead poisoning

1. **CNS: insomnia, nightmares, irritability, anxiety, anemia, kidney**
2. **Car exhaust is organic**

Mercury (Summary)

Chronic mercury poisoning

1. **CNS effects**:
   a) **Mercury vapor (elemental mercury): largely neuropsychiatric: depression, irritability, shyness, insomnia, emotional instability, forgetfulness, confusion, excessive perspiration, uncontrolled blushing (erethism) and tremors**
   b) **Methylmercury**
      1) **Paresthesia (abnormal spontaneous sensation, ex. tingling)**
      2) **Visual changes (constriction of visual field)**
      3) **Hearing defects**
      4) **Dysarthria (speech disorder)**
      5) **Ataxia (unstable gait, coordination, loss of muscle movement)**
      6) **Fetus is extremely susceptible**
   c) **Inorganic mercury: little known**

1. **Kidney: target organ of inorganic mercury toxicity**
   a) Organomercurials-high fetal toxicity

Other Metals

A. Aluminum

1. **Low toxicity, aluminum hydroxide is antacid**
2. **Shaver's disease – by inhalation in industry – lung fibrosis**

B. Antimony: toxicity similar to arsenic, garlic breath

C. Beryllium

1. **Mining**
2. **Berylliosis / granuloma**

D. Chromium

1. **Necessary for glucose metabolism (trivalent)**
2. **Insoluble hexavalent cause lung cancer by inhalation**

Other Metals

E. Cobalt
1. Essential element in vitamin B_{12}
2. Polycythemia (increase in RBC)
3. Goiter
4. Cardiomyopathy – beer drinkers

F. Copper
1. Essential element
2. Wilson's disease (hereditary, retains copper)
3. Metal fume fever

G. Fluoride
1. Reduces dental caries at 0.7-1.2 mg/1 or ppm
2. Dental fluorosis (discoloration and/or pitting) in children above 2 ppm
3. Brittle bones at higher concentrations
4. Discolors leaves

Other Metals

H. Iron, Fe_2O_3
1. Metabolic acidosis – cell death through hemosiderin

I. Manganese
1. Manganese pneumonitis
2. CNS: Parkinson's disease

J. Metal fume fever - ZnO, MgO, CuO

K. Nickel
1. Dermatitis (nickel itch, jewelers itch)
2. Nickel carbonyl ($Ni[CO]_4$) – carcinogenic, highly acutely toxic, pneumonitis leukocytosis, temperature, delirium
3. Nickel subsulfide – carcinogen in humans (nose)

Other Metals

L. Phosphorus
1. Used in matches, rat poisons, fireworks
2. GI upset – vomitus may be phosphorescent
3. Liver injury – jaundice
4. Chronic – necrosis of bone "phossy jaw," Alice Hamilton

M. Selenium
1. Essential (glutathione peroxidase)
2. Excess in livestock – "blind staggers or alkali disease" characterized by lack of vitality, loss of hair, sterility, atrophy of hooves, lameness and anemia
3. Excess in humans – discolored/decayed teeth, skin eruptions, GI distress, partial loss of hair and nails, garlic breath
4. Liver injury

N. Silver
1. Skin – argyria (blue skin)

Other Metals

O. Thallium
1. Rodenticides, ant poison (discontinued many countries)
2. Distributed like potassium, mining
3. GI irritation – acute
4. Alopecia

P. Uranium
1. Kidney injury

Q. Zinc
1. Essential
2. Acute oral toxicity: vomiting, diarrhea, fever
3. Inhalation: metal fume fever - fever

Solvents and Vapors

Halogenated Hydrocarbons

(low flammability, excellent solvents)

- **Acute – CNS depression, defatting skin, myocardium**
- **Chronic – liver, kidney**
- **Chlorinated – solvents (CNS/skin/cancer)**
  CCl_4-carcinogenic, liver, kidney
- **Brominated – fumigant, solvents (CNS/skin)**
- **Fluorinated – refrigerants (ozone layer/myocardium)**

Structure Affects Activity

- **Useful, but dangerous – i.e., guilty by association, e.g., C_4F_8**
- **Branched chain isomer – lethal @ 0.5ppm**
- **Linear isomer – lethal @ 6,100ppm in 4 hr**
- **Cyclic isomer – essentially non-toxic**

Aromatic Hydrocarbons

- **Benzene – CNS depression, leukemia**
- **Toluene – CNS depression (glue sniffers)**
- **Styrene – dermatitis, CNS depression**

- **Poly-aromatic hydrocarbons – doxin, PCBs, biphenyls – liver/thyroid/skin**
- **Nitrobenzene – CNS, jaundice (liver effect), methemoglobin - blue lips & fingernails**

- **Phenol – CNS, liver, kidney, skin effects**
  (absorbed readily through skin)

Aliphatic Alcohols

- **Methanol – alcohol dehydrogenase-blindness-treat with ethanol**
- **Ethanol – CNS depression, fetal alcohol syndrome, liver cirrhosis**
- **Isopropanol – CNS depression, gastritis**

Glycol Ethers

Ethylene glycol monomethyl ether (EGME)
$CH_3OCH_2CH_2OH$

1. Disrupts sperm development
2. Developmental toxin – day 7,8-neural tube; day 10-11-digit/paw effects, brain, liver, and kidney

Ethylene glycol monoethyl ether (EGEE)
$CH_3CH_2OCH_2CH_2OH$

1. Testicular degeneration
2. Reproductive/developmental toxins, but less severe

Propylene glycol monomethyl ether (PGME)

– Not a reproductive/developmental toxin

Ketones

- **Acetone (dimethyl ketone) – CNS, skin effects**
- **Methyl ethyl ketone – CNS, skin, reproductive and developmental effects**
- **Methyl butyl ketone – CNS and peripheral nervous system effects**

Pesticides

- **Organophosphates – cholinesterase inhibitor; parathion, dursban, dichlorvos,**
- **Organochlorine – CNS; DDT, aldrin, kepone, mirex**
- **Carbamates – reversible cholinesterase inhibitor; sevin**
- **Chlorophenoxy – liver, kidney, CNS; 2,4-D, agent orange, 2,4,5-T**
- **Pyrethrins – CNS effects; resmethrin**

Occupational Exposure Limits (OELs)

Requirements, Recommendations, and Guidelines

Goals of OELs

- Control health effects of exposures to "agents" (chemical, biological, physical).
- Designed to protect workers against adverse health effects day-after-day.
- Applies only to the traditional workplace.

Healthy Worker Syndrome

OELs are set for:

Healthy, young, male workers

Able to report for work every day

Work 5 days of 8 continuous hours work per week

Based on data that varies widely in accuracy and age

Presumed to be an adequate margin of safety

Exposure is Affected by:

- **Genetics**
- **Age**
- **Personal habits**
  - **Smoking**
  - **Alcohol**
  - **Drugs**
- **Medication**
- **Previous Exposure**
- **Environmental Exposure**

Basis for Setting OELs

Paracelsus (~1500) said – "all substances are poisons… only the dose differentiates a poison from a remedy"

- **Human use and experience**
  - Epidemiological data
  - Medical case histories
  - Human exposure data on adverse effects
- **Long term animal toxicity studies**
  - Best for chronic toxicity and carcinogenicity
- **Short term animal toxicity studies**
  - Dermal data on skin penetration
  - Basis for STEL or Ceiling Limit

Basis for Setting OELs

Special animal studies:

- **Genetic toxicity**
- **Developmental/reproductive toxicity**
  - **Unique hazard (e.g., thalidomide)?**
  - **Male or female reproductive performance?**
- **Metabolism/pharmacokinetics**
  - **Absorption, distribution, fate and elimination**
- **Physical/chemical properties**

Animal Toxicology Information

- Route of exposure
- Route of administration
- Species tested
- Chemical/physical/biological factors
- Test material
- Dose, route, frequency, concentration, duration
- Genetic factors
- Immunologic and dietary factors
- Gender, age and emotional status

Extrapolation of Animal and Other Data

- **Application of known data and/or experience to areas not known.**
- **Based on assumptions**:
  - **Continuity**
  - **Parallelism between what is known and unknown.**

Exposed Dose vs. Absorbed Dose

- **Exposed Dose:**
  Amount of substance which a given organism is exposed, expressed as:
  - parts per million (ppm) for gases & vapors
  - milligram per cubic meter (mg/m^3) for solids
  - Fibers per cubic centimeter (fibers/cc) for fibers
- **Absorbed Dose:**
  Amount of substance deposited in or absorbed by an organism, expressed as:
  - mg/kg

Occupational Exposure Limits (OEL)

OELs are country specific and variously know as:

- **PEL – Permissible Exposure Limits –** OSHA, USA, required legal limits.
- **REL – Recommended Exposure** Limits **–** NIOSH, USA, recommendations.
- **TLV® – Threshold Limit Values® –** ACGIH, USA, recommendations
  - **(OSHA adopted 1968 TLV list – PELs)**
- **WEEL – Workplace Environmental Exposure Limits –** AIHA, USA, recommendations.
- **MAK – Maximium Workplace Concentrations –** German, required legal limits.
- **BEI® – Biological Exposure Indices –** ACGIH, USA, recommendations.

Permissible Exposure Limit (PEL)

- **Legal US exposure limit** to control health effects from exposures to “agents.”
- Protect workers day-after-day without adverse health effects.
- Applies only to workplaces covered by US OSHA.

Action Levels and Policies

- **Action Level (usually ½ PEL)**
- **Other US OSHA Policies**
  Carcinogens
  - **Zero tolerance**
  - **No known safe exposure level**

TLV® Definitions

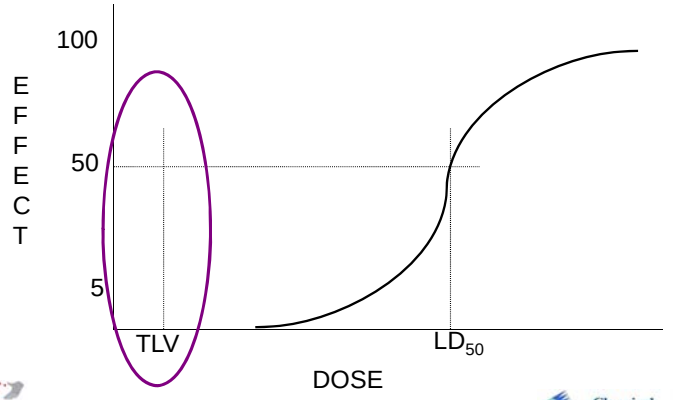
Threshold limit values refer to:

… airborne concentrations of substances and represents conditions under which it is ***believed that nearly all workers may be repeatedly exposed day after day without adverse health effects*****.**

… a small percentage of workers may experience discomfort from some substances at concentrations at or below the threshold limit.

… may be affected more seriously by aggravation of a pre-existing condition or by development of an occupational illness.

Threshold Limit Values (TLV)



Categories of TLV's

AIR CONTAMINANTS

- **Time-weighted average (TWA)**
- **Short-term exposure limit (STEL)**
- **Ceiling value (C)**

- **TLV Range:**
  HIGHEST
  - Carbon dioxide - 5000 ppm

  LOWEST
  - Osmium tetroxide - 0.0002 ppm

TLV Limitations

- **Not** a relative index of toxicity.
- **Not** intended to apply to general public.
- **Not** for exposures >8 hr/day; 40 hr/wk.
- **Not** used as proof of hazard.
- ***Not for other countries with different working conditions*****.**

Biological Exposure Indices (BEIs®)

- **BEIs are indications of a person's "uptake" of a substance.**
  - **Chemical, metabolite, characteristic or reversible biochemical change**
    - Urine, blood, exhaled air
  - **Represent levels observed in healthy workers exposed at the TLV.**
    - Not always the case…e.g. lead, based on health effect.
  - **Indirectly reflects dose**
  - **Not a measure of adverse effects or diagnosis of illness**
  - **Not a distinction between hazard and non-hazard.**

Biological Exposure Indices (BEIs)

- **BEIs can assist CHHO Professionals:**
  - » Used as a guideline
  - » Apply to 8 hr day, 5 day week
    - – Adjustment to irregular work schedules is not recommended
  - » Detect and determine absorption by skin or GI
  - » Assess body burden
  - » Reconstruct past exposure in absence of exposure data
  - » Test efficacy of PPE and engineering controls
  - » Monitor work practices
- **BEI does not indicate need for biological monitoring.**

Working with BEIs

- **Sample collection time is very important.**
- **Sample acceptability:**
  - » Reject highly diluted or concentrated urine samples.
- **Sample collection requires proper quality assurance.**
  - » Include blind challenges to assess lab capability.
  - » B – background (may be present in unexposed)
  - » Nq – non-quantitative
  - » NS – nonspecific (observed with other chemicals)
  - » Sq – semi-quantitative (interpretation may be ambiguous)

BEIs vs. TLVs

- **BEIs – Index of uptake**
  - » Uptake may vary between workers.
  - » Measurement on a person
- **TLVs – indicate potential for inhalation exposure**
  - » Measurement on an environment
- **Inconsistencies between BEIs and TLVs due to:**
  - » Physiological makeup and health status
  - » Occupational exposure factors
  - » Non-occupational exposure factors
  - » Sampling location
  - » Particle size distribution
  - » Effectiveness of PPE or controls

Classification Schemes

ACGIH CARCINOGEN

- **A1 Confirmed human carcinogen**
  - » Human data
- **A2 Suspected human carcinogen**
  - » Animal data due to conflicting or insufficient human data
- **A3 Animal carcinogen**
  - » Not relevant for extrapolation to humans

Classification Schemes

ACGIH CARCINOGEN

- **A4 Not classified as a human carcinogen**
  - » Inadequate data
- **A5 Not suspected as a human carcinogen**
  - » Good negative human
  - » Considers animal data

NOTE: If no data exists, compound remains unclassified

Time Weighted Average (TWA)

- **Average exposure for an individual over a working period of time, determined by taking one or more samples during the working period:**

$$\text{TLV-TWA}^* = \frac{C_1T_1 + C_2T_2 + \ldots + C_NT_N}{T_1 + T_2 + \ldots + T_N}$$

Where:
C = airborne concentration
T = time

*** A TLV expressed as a TWA**

8-Hr Time Weighted Average

- **Average exposure for an individual over an 8-hr working period of time, determined by taking one or more samples during the 8-hr working period:**

$$\text{TLV-TWA}_8 = \frac{C_1T_1 + C_2T_2 + \ldots + C_NT_N}{8 \text{ hrs}}$$

Example 1

A degreaser operator is monitored for exposure to Stoddard solvent. The monitoring data is:

TIME PERIOD (NUMBER)	*CONCENTRATION (PPM)*	*TIME (HOUR)*
1	80	2
2	110	4
3	55	2

Solution

$$\text{TLV-TWA}_8 = \frac{C_1T_1 + C_2T_2 + \ldots + C_NT_N}{8 \text{ hrs}}$$

$$\text{TLV-TWA}_8 = \frac{(80 \times 2) + (110 \times 4) + (55 \times 2)}{8 \text{ hrs}}$$

EIGHT HOUR TLV-TWA = 89 ppm

Over exposed?
(TLV = 100 ppm)

Example 2

Consider the same example with no exposure for the last two hours:

TIME PERIOD (NUMBER)	CONCENTRATION (PPM)	TIME (HOUR)
1	80	2
2	110	4
3	0	2

Solution

$$\text{TLV-TWA}_8 = \frac{C_1T_1 + C_2T_2 + \ldots + C_NT_N}{8 \text{ hrs}}$$

$$\text{TLV-TWA}_8 = \frac{(80 \times 2) + (110 \times 4) + (0 \times 2)}{8 \text{ hrs}}$$

EIGHT HOUR TLV-TWA = 75 ppm

Unit Concentration

$$\text{TLV (ppm)} = \frac{\text{TLV (mg/m}^3\text{)} \; 24.45}{\text{(molecular weight)}}$$

$$\text{TLV (mg/m}^3\text{)} = \frac{\text{TLV (ppm) (MW)}}{24.45}$$

TLV - Short Term Exposure Limit (STEL)

- **A 15-minute TWA exposure.**
- **No more than 4 times per day, with at least 60 minutes between.**
- **Should not be exceeded anytime during workday, even if 8-hour TWA is within TLV-TWA.**

Excursion Limit (without STEL)

- **Excursions in worker exposure levels may exceed 3 times the TLV-TWA for no more than a total of 30 minutes during a workday.**
- ***Under no circumstances* should they exceed 5 times the TLV-TWA, provided the TLV-TWA is not exceeded.**
  - **Applicable to TLV-TWAs that do not have STELs**

Other TLV Notations …

- "Skin" potential exposure by the cutaneous route, including mucous membranes and the eyes.
- "SEN" potential to produce sensitization.

Unusual Work Schedules

Application of TLVs to unusual work shifts:

Different from 8-hour day, 40-hour week

Requires judgment.

OSHA model Modified PEL

$$PEL_{modified} = PEL \frac{8\ (hours)}{T\ (hours)}$$

T > 8 Hours

Example

- **1,1,2-trichloroethane has a biologic half-life of 16 hours in people. What modified TLV or PEL is appropriate for persons who want to work 3 days at 12 hours per day for the work week?**
- **The ACGIH TLV & OSHA PEL for 1,1, 2-trichloroethane is 10 ppm.**

$$PEL_{modified} = 10 \frac{8\ (hours)}{12\ (hours)} = 6.66\ ppm$$

Mixtures

If the biological effects of mixture components are additive:

$$\frac{C_1}{T_1} + \frac{C_2}{T_2} + \ldots + \frac{C_N}{T_N} = K$$

Where:

C_N = Measured TWA concentration

T_N = TLV for a substances

If k is **<** 1, combined exposure is less than TLV

If k is **>** 1, combined exposure exceeds the TLV

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Break

Chemical Spill Response and Clean-up

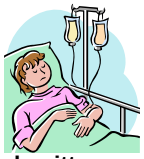
Size of spill determines response

Emergency Notification and Response

- The notification and emergency response procedure for accidents and incidents should be written and understood by everyone.
- A rapid and effective response helps insure injured persons receive rapid and correct medical attention and/or that incidents are quickly contained and controlled, and that effects and damage to people, facilities, the environment and the community are minimized.

Chemical Spill Response Medical Treatment

- Employer should provide the following medical services in emergencies:
  - Medical examination after exposures
  - If exposures are above required/regulated levels of exposure
  - Follow-up exams as necessary
- Employer should provide to the physician:
  - Identity of chemical
  - Description of exposure conditions
  - Description of signs and symptoms of exposure
- Employer and victim should obtain a confidential written report from the examining physician

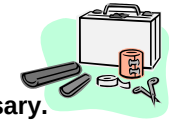


Chemical Spill Response Record Keeping

- Maintain accurate records of accidents/incidents response.
  - All involved personnel
  - Exposure measurements
  - Medical examination, consultations
  - Medical tests
  - Medical follow-ups
- Records should be confidential and protected from unauthorized disclosure.
- Records should be shared with victim.
- Records should be examined for patterns.

Chemical Laboratory First Aid

- First aid kits for minor injuries should be centrally located and available in or nearby each laboratory.
- Use for minor accidents/incidents.
- Determine if medical attention is necessary.
- Immediately notify proper authorities, if necessary or in doubt.
- Determine if chemical exposure occurred.
- If necessary, take immediate preventative action to make lab safe, e.g., shut down reactions, electricity, etc.



Chemical Laboratory First Aid

Wounds:

- If bleeding is profuse, apply steady, direct pressure over the wound using a sterile dressing, if possible, or clean cloth.
- Keep the wound as clean as possible.
- Remove or cut away any clothing covering the wound.
- Flush with water to wash out loose dirt and debris.
- Do NOT try to remove foreign matter embedded in the wound
- If there is an impaled object, Do NOT try to remove it. Efforts to do so may cause severe bleeding and further damage.
- Control bleeding by direct pressure, but do not apply pressure on the impaled object itself or on immediately adjacent tissues.
- Stabilize the impaled object with a bulky dressing.

Chemical Laboratory First Aid

Thermal Burns:

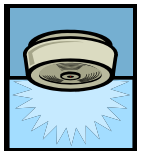
- Immerse burned area in cold water or apply cold compresses for 30 minutes
- Do NOT attempt to rupture blisters on the burn

Chemical Laboratory First Aid

- Chemical Burns:
  - Speed is essential.
  - Consult chemical labels & MSDS for special instructions.
  - Flush burn area immediately with water for 15 minutes.
  - Taking care not to spread the chemical, remove any clothing, especially shoes and socks, that may be contaminated.
  - Do NOT use salves, ointments, cream, sprays, or any other covering except for chemical-specific remedies such as for HF or phenol.
  - Do NOT attempt to rupture blisters over the burn.
- If chemicals splashed into the eyes:
  - Flush the affected area with water for a minimum of 15 minutes.
  - Remove contact lenses, if present, as rapidly as possible, since they prevent water from reaching the cornea.
  - Eyelids may have to be forced open so eyes can be totally flushed.
  - If large particles are in the eye, an eye wash should not be used.
  - Do NOT use salves, ointments, cream, sprays, or any other covering except for chemical-specific remedies such as for HF or phenol.

Spill Cleanup Preparation

- Emergency Equipment
  - Internal communication/alarm system
    - Telephones (Label all phones with emergency numbers)
    - Alarm pull boxes
  - External communication/alarm system
  - Fire extinguishers
  - Emergency eyewash and showers
  - Spill stations



Spill Cleanup Preparation

- **Knowledge Needed**
  - Location of emergency electrical circuit breakers, shutoff valves, switches, disconnects for building, area, laboratory, room, equipment
  - Response procedures for personal injuries/ exposures and emergencies
  - Emergency evacuation routes (posted)

Spill Cleanup Preparation

- **Maintain Current Safety Data Sheets**
  - Attention to:
    - Chemical hazards
    - First aid information
    - Spill response
    - Firefighting information
    - Engineering controls
    - Stability and reactivity
    - Proper storage
    - Disposal considerations

Spill Cleanup Preparation

- **Maintain complete Spill Kits**
  - Absorbent material
    - Absorbent pillows or powders
    - Activated carbon for organic solvents
  - Neutralizing agents
    - Acid Neutralizers –e.g., sodium bicarbonate ($NaHCO_3$) powder
    - Base Neutralizers-e.g., citric acid powder
    - Solvent Spills-activated carbon

Spill Cleanup Preparation, cont'd.

Spill Kit should also contain:

- Personal Protective Equipment (PPE)
  - 2 pairs of chemical splash proof goggles
  - Several pair of disposable gloves
  - Disposable, charcoal (volatile, aerosol) respirators
  - Disposable aprons or jump suits
  - Disposable shoe covers (for floor spills)

Spill Cleanup Preparation

- **Additional cleanup equipment:**
  - Plastic pail/bucket(s) with lids (large enough to contain spill and cleanup material)
  - Plastic dust pan
  - Broom or brush
  - Plastic bags
  - Sealing tape
  - pH paper
  - Sign(s):
    Danger Chemical Spill
    Keep Out

Spill Cleanup Preparation

SCBA Respirators

- Two persons are required to use a Self Contained Breathing Apparatus (SCBA)
- One person stands-by to rescue/assist the other in case of a problem
- Never rely on a single SCBA
- Never use a SCBA alone
- SCBAs must be well maintained and inspected weekly if they are part of the safety program

Spill Cleanup Preparation Risk Assessment

(Anticipation)

- What is the worst thing that could happen if a chemical was dropped/spilled, etc.?
  - inconvenience
  - skin burns
  - fire
  - explosion
  - chemical exposure (fatality; injury, permanent, temporary)
- Know the worst case scenario for a spill.
- How you would respond to a spill, emergency situation?
- What are the appropriate clean-up and decontamination procedures?

Spill Cleanup Preparation Risk Assessment

Estimating Potential Hazards (Evaluation)

- What are the chemical, physical and toxicological properties of the chemicals you are using?
- What is the amount of chemical?
- What are your knowledge and skills?
- What are possible locations/conditions of a spill, accident?
- Ask for assistance if you are unsure

Spill Cleanup Preparation Risk Assessment

Chemical Toxicity (Evaluation)

- Route of exposure
- Acute toxins
- Acids and corrosives
- Lachrymators, irritants and allergens
- Carcinogens, repro-toxins, etc.
- Biohazardous, radioactive material

Spill Cleanup Risk Assessment

Chemical Flammability (Evaluation)

- Hazardous locations
- Ignition sources
- Presence of other flammables
- Store excess flammables in flammable storage cabinets
  - Use external flammable storage rooms for large quantities.

Spill Cleanup Prevention

(Control)

- Eliminate clutter
- Purchase only amount of chemical required
- Understand work practices and procedures
- Use unbreakable secondary containers
- Store chemicals properly
- Dispose of waste and excess chemicals properly and timely

Cleanup Responsibilities

- **Laboratory Staff:**
  - Ensuring timely spill reporting and cleaned up
  - Cleaning up nuisance spills in their area, even if someone else spills them (janitors, service people)
  - Knowing the properties of what they work with
  - Taking reasonable steps to prevent spills
- **Specially trained Safety Cleanup Team:**
  - Assist researchers not comfortable cleaning up spills (including nuisance spills)
  - Clean-up serious/major spills

Nuisance Spills

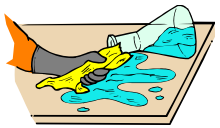
- **Spills of < 4L of known hazard, that you are comfortable cleaning up**
  - **Assess the hazard**
  - **Wear appropriate PPE**

- **If unsure or need assistance with PPE selection or cleanup, call the Safety Cleanup team.**

Nuisance Chemical Spill Cleanup Procedure

- Alert people in immediate area
- Post area
- Confine spill
- Absorb excess, surround area with absorbent material
- Wear appropriate PPE
- Avoid breathing aerosols
- Use forceps, etc., to pickup broken glassware, etc.
- Work from outer edge toward center to cleanup
- Do not dry sweep
- Clean spill area with soap & water, specific solvent or neutralizing material (if known)
- Collect contaminated absorbent, gloves, residues in plastic bag(s)
- Label, with chemical name if possible, and dispose of waste properly

Potentially Hazardous Spills



- **Spills of > 4L or**
- **Smaller spills of:**
  - **Low LD_{50} (high acute toxicity)**
  - **Carcinogens, repro-toxins, etc.**
  - **Flammable liquids or metals**
  - **Chemicals of unknown toxicity or hazards**

Potentially Hazardous Chemical Spill Cleanup Procedure

- Attend to injured/contaminated or exposed individuals.
- Remove persons from the exposure without endangering yourself.
- Alert persons in the immediate area to evacuate.
- Consider people with disabilities.
- If spill is flammable, turn off heat and ignition sources (if possible).
- Call Emergency Phone Number to report incident.
- Post area—**Danger, Keep Out! Hazardous Chemical Spill**
- Close doors to affected area.
- Locate MSDS.
- Assist Specialized Safety Cleanup personnel if you are knowledgeable about the spill.

Only trained personnel should do cleanup!

Mercury Exposure and Cleanup

- **Mercury metal exposure can cause severe health problems:**
  - **Tremors**
  - **Changes in vision or hearing**
  - **Insomnia**
  - **Weakness**
  - **Memory difficulty**
  - **Headaches**
  - **Irritability**
  - **Nervousness or shyness**
  - **Acrodynia (painful extremities) - *a condition caused by chronic exposure to mercury***

Mercury Exposure & Prevention

- **Routes of exposure**
  - **Inhalation**
    - **Main hazard**
    - **Evaporates releasing hazardous vapors**
  - **Skin absorption**
- **Personal Protective Equipment Required**
  - **Nitrile gloves**
  - **Safety glasses**
  - **Closed-toed shoes**
  - **Lab coat**

Mercury Spill and Exposure

- **Preparation is critical.**
- **Substitution/elimination is the best prevention.**
- **All mercury spills, including those from broken laboratory thermometers and manometers, should be cleaned up immediately.**

Mercury Spill Prevention

- **Trays should be used under equipment where mercury is used.**
- **Mercury beads, splashes, and rolls around.**
- **Prevent mercury from entering cracks, crevices, and drains.**
- **Cease activities.**
- **Secure spill area, contain mercury spill area.**
- **Restrict area until entire spill is cleaned up.**
- **Do not walk in spill area.**
- **Evacuate room via route away from spill.**
- **Lower room temperature to reduce evaporation.**

Mercury Spill Cleanup

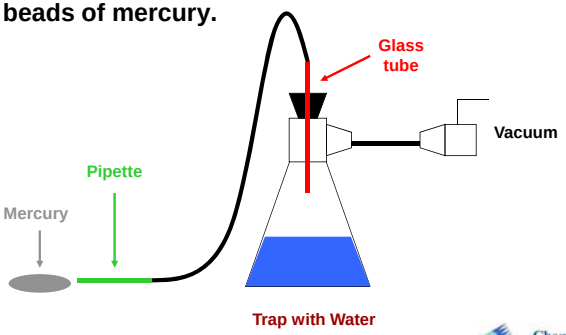
- Spill powders can be used as temporary controls:
  - Commercial spill kits are available
  - Or mix 85 grams of finely powdered sodium thiosulfate with 15 grams of powdered EDTA

Mercury Spill Cleanup

- Cover spill from perimeter toward the center.
- Remove debris:
  - Dispose of as hazardous waste and cleanup material (gloves, towels, etc).
  - All waste should be placed in labeled, sealed, leak-proof, containers.
  - Never dispose of mercury waste in sewer system.
- Special vacuum cleaners designed to pick up mercury safely are available for cleanup.
- NEVER sweep up spill or use a regular vacuum.

Other Mercury Spills Cleanup Equipment

- A side-arm flask connected to a vacuum pump or sink aspirator can be used to vacuum up small beads of mercury.



Mercury Spill Cleanup Special Precaution

- Special attention should be given to cleaning cracks and crevices where the mercury beads may have settled.

Mercury Spill Cleanup Special Precautions

- Large spills
- Spills in confined areas with poor ventilation
- Spills in areas heated above room temperature
- Should be cleaned up by trained personnel with protective equipment
- There is a risk of high exposure to mercury vapors in these situations.

Fire Protection and Prevention in Chemical Laboratories

Fires

- Preventable
- Caused by unsafe practices
  - Electrical safety violations
  - Uncontrolled use of flammable and combustible materials
- Control
  - Inspect, inspect, inspect

  Educate, educate, educate!

Home Fires

1 million fires and 8,000 deaths annually in the US

Leading causes:
Cigarettes
Heating/cooling equipment
Electrical
Matches, lighters, candles

Industrial Fires

- **Fifth leading cause of accidental death**
  - Vehicles, falls, poison, drowning, fire
- **Most dangerous industries from fire hazard:**
  - Mines
  - Grain elevators and mills
  - Refineries
  - Chemical plants
- **Leading causes:**
  - Electrical
  - Smoking
  - Friction
  - Overheating
  - Hot surfaces

Key Elements of Fire Safety

Get occupants out

Minimize property loss and interruption

Fire Containment/Suppression

Common Myths

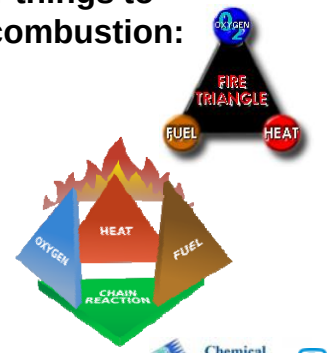
- **Fire will light the way out**
  - Smoke cloud & soot
- **Plenty of time to escape**
  - 1 min from small to inescapable fire
- **People are killed by the flames**
  - #1 killer in fires is CO, not flames
- **Wait to be rescued**
  - No! Act to save self
  - Ladders can reach to about 6th floor
- **Can not prepare for a fire**
  - Preparation can save your life

It's the Smoke…

Facial Burns

Fire

- **A fire must have four things to ignite and maintain combustion:**
  - **Fuel**
  - **Heat**
  - **Oxygen**
  - **Chain reaction**



Flash Point

- **Flash point:**
  - The minimum temperature at which a liquid gives off enough vapor to form an ignitable mixture.
  - In general, the lower the flash point, the greater the hazard.
- **Flammable liquids:**
  - have flash points below 38ºC
  - are more dangerous than combustible liquids
  - may be ignited at room temperature
- **Combustible liquids:**
  - have flash points at or above 38ºC
  - Can pose serious fire and/or explosion hazards when heated

Flammability/Explosive Limits

Above UFL/UEL, mixture is **too rich to burn**

Upper Flammability/Explosive Limit (**UFL/UEL**)

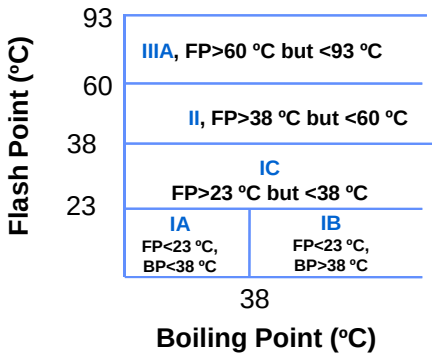
Flammability/Explosive Range

Lower Flammability/ Explosive Limit (**LFL/LEL**)

Below LFL/LEL, mixture is **too lean to burn**

Defined in terms of the amount of fuel in air.

Classes of Flammable and Combustible Liquids



OSHA Office of Training and Education, defined in Fahrenheit

Classes of Some Flammable Liquids

	Common Name	Flash Point (°C)
CLASS IA	Ethyl Ether	- 45
CLASS IB	Gasoline	- 43
	Methyl Ethyl Ketone	- 6
	Toluene	4
CLASS IC	Xylene	27 - 46
	Turpentine	35

OSHA Office of Training and Education

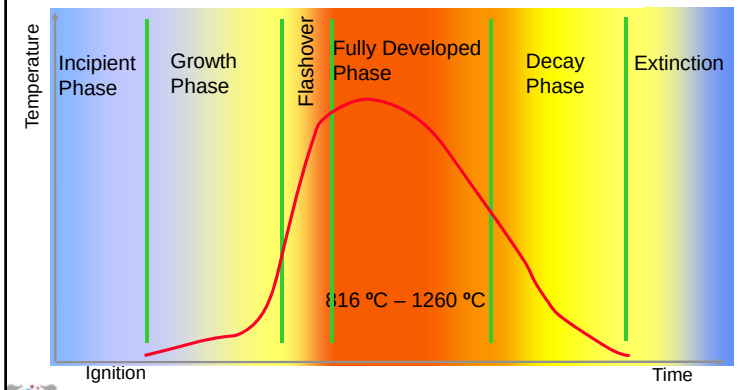
Fire Safety Program Components

A good plan for safe use of flammable and combustible liquids contains at least these components:

- **Control of ignition sources**
- **Proper storage**
- **Fire control**
- **Safe handling**

OSHA Office of Training and Education

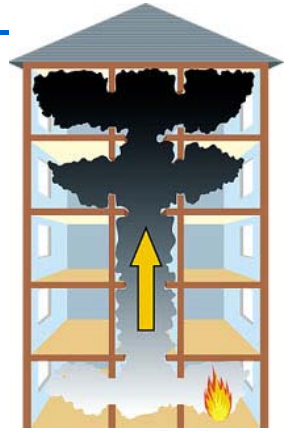
Fire Behavior



Fire Behavior

- Hot expanding gases move vertically
  - Tightness of construction
  - External winds
  - Internal/external temperature
  - Vertical openings
    - Stairways
    - Elevator shafts
    - Ventilation shafts

Stack Effect



Vapor Volume

Volume of gas formed when a liquid substance evaporates

Computed from specific gravity and vapor density

$$\text{Vapor Volume } (m^3/\text{liter}) = \frac{0.829\ (\text{SpG})}{\text{Vapor density}}$$

Example: What is the vapor volume of a liter of acetone?
[SpG = 0.9, relative to water; Vapor density = 2, relative to air]

$$\text{Vapor Volume } (m^3/L) = \frac{0.829\ (0.9)}{2} = 0.373\ m^3/L$$

Vapor Volume

What is the probability of forming a combustible mixture if a 4 liter container of acetone is used in a room 3 x 4 x 2.5 m?

[LEL = 2.5%; assume incomplete mixing factor 5]

Volume of the space = 30 m^3

Vapor volume = 0.373 m^3/L

Vapor volume necessary to form a Combustible mixture:

30 m^3 x 0.025 = 0.75 m^3

$$\frac{0.75\ m^3}{0.373\ m^3/L} = 2.01\ L$$

Applying the mixing factor of 5:

2.01 L / 5 = 0.40 L

[About = 1 coffee mug]

Since it doesn't take much more than "1 coffee mug" of acetone to form a combustible mixture, the probability appears to be high!

Housekeeping…

Flammable Liquid Containers

Tool Cleaning (Acetone)

Fire Hazards

- **Sources of fuel**
  - Flammable liquids
  - Flammable gases
  - Wood, paper, cardboard
  - Oil soaked rags

Train employees to notice & report fire hazards

Periodic inspections

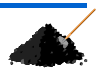
Drills

- **Sources of heat (ignition)**
  - Electrical circuits:
    - Shorts, sparks
    - Arcs (switches)
    - Heat build-up
  - Hot surfaces
  - Space heaters
  - Hotplates, coffee pots, coffee makers
  - Welding
  - Smoking
  - Open flames
  - Static electricity

Classification of Fires

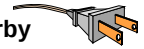
With recommended extinguisher distances

- **A** **Ordinary combustibles – cloth, paper, wood, coal** **~23 m**



- **B** **Flammable/combustible liquids, gases, greases and oils - gasoline, diesel fuel** **~15 m**

- **C** **Energized Electrical equipment cables, motors** **nearby**



- **D** **Combustible metals - sodium, magnesium, titanium** **~23 m**

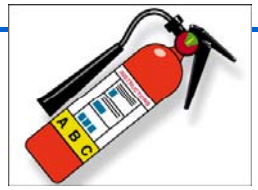
- **K** **Restaurant grease fires associated with cooking** **nearby**

Classification of Fires

- **A** Extinguish by cooling or smothering.
  (water)
- **B** Extinguish by inhibiting release of combustible vapors or interfering with the chemical reaction-release of OH radicals.
  (CO_2 or dry powder: monoammonium phosphate)
- **C** Extinguishing agent must **not** be conductive.
  (CO_2 or dry powder)
- **D** Extinguishing agents must absorb heat and not react with the metal.
  (special dry powder, sand)
- **K** (Special liquid chemicals)

Fire Extinguishers

Dry Chemical



CO_2

Water

Placed within ~15-25 m

Annual & Monthly inspections

Large Fire Extinguisher

Fire Extinguishers

Fire Alarm Systems

- **Will it be recognized and followed?**
  - Audible, visual, public address systems…
- **What about deaf or blind employees?**
  - Are there "dead spaces"…
- **System reliability**
  - System failure may not be obvious
  - Supervised systems (built-in monitoring)
  - Testing, maintenance and backup systems

Fire Detection & Alarms

- **Thermal**
- **Heat**
  - Fixed temp
  - Rate of rise
    - ~6 to 8 C/min (12 to 15ºF/min)

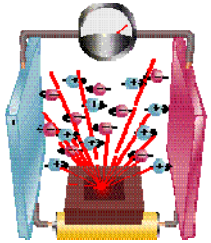
Issues:

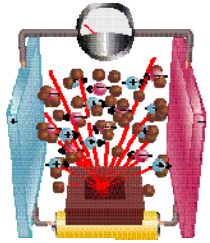
Testing

Dust, corrosion, hot processes, weather, mechanical damage

- **Smoke**
  - Photoelectric
    - IR from smoke
  - Ionization
    - Ionize smoke
- **Flame Detectors**
  - Flames – IR or UV
- **Gas Sensors**

Smoke Detectors





- Alpha particles from Americium-241 (red lines) ionize the air molecules (pink and blue spheres).
- The ions carry a small current between two electrodes.
- Smoke particles (brown spheres) attach to ions reducing current and initiate alarm.

False Alarms

False alarms may be triggered by construction dust created during renovations

Manual Pull Stations

- Manual Pull Stations are devices located on the wall (usually near an exit)
  - Sends a signal to the building's fire alarm system when activated
  - Places the building into alarm

People are reluctant to sound fire alarms!

Responding To A Fire

Employee Training

Few employees know how to effectively use extinguishers!

Need for training:
- Initial training
- Annual refresher

Emergency Response (phone numbers)

Using a Fire Extinguisher

P Pull
A Aim
S Squeeze
S Sweep

Video Courtesy of Washington State Emergency Management Division, Public Education Program

Water

- Water is highly effective on Class A fires, by cooling down the fire and surrounding atmosphere.
- Water is usually available.
- It can be used to cool down the firefighting team to prevent heat exposure.

Disadvantages

- Water should NOT be used to control a B or C fire.
- Inadequate pressure or too high pressure can cause problems.
- The volume of water can be restricted by the length of water lines and hoses (frictional loss ~3500 Pa for every 3 meters of 4 cm diameter hose).
- The fire nozzle can clog due to non-filtered materials in the lines.
- Hydrogen can be produced if water is applied to very-hot fires.

Electrical Fires

Pull the plug out or switch off the power at the fuse box. This may stop the fire immediately.

Smother the fire with a fire blanket, or use a dry powder.

Never use water on it.

WHAT TO DO IF SOMEONE CATCHES ON FIRE

If you should catch on fire:

STOP - where you are
DROP - to the floor
ROLL - around on the floor

This smothers the flames, possibly saving your life.

Remember **STOP, DROP and ROLL**

If a co-worker catches on fire:

Smother flames by grabbing a blanket or rug
Wrap them in it.
Could save them from serious burns or death.

WHEN NOT TO FIGHT A FIRE

Don't fight a fire, when:

- It is bigger than a waste paper bin
- One extinguisher is not enough
- The fire is spreading beyond the spot where it started
- Smoke is affecting your breathing
- You can't fight the fire with your back to an escape exit
- The fire can block your only escape
- You don't have adequate fire-fighting equipment

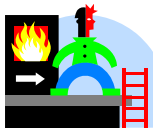
DON'T FIGHT THE FIRE YOURSELF

CALL FOR HELP

Remember

When…

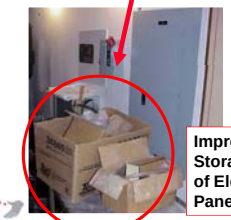
- The extinguisher runs out of agent
- Your path of escape is threatened
- The extinguisher proves to be ineffective
- You are no longer be able to safely fight the fire



…LEAVE THE AREA IMMEDIATELY!

Storage Guidelines

- All storage must be at least 1 m from electrical panels. In some emergency situations it will be necessary to access these panels quickly.



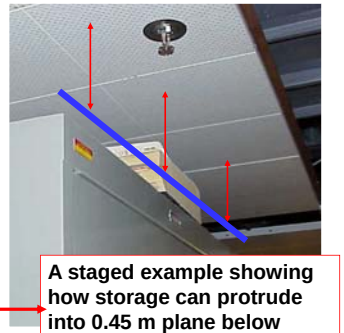
Improper Storage in front of Electrical Panel

- Maintain at least 1 m clearance from heating surfaces, air ducts, heaters, and lighting fixtures.
- Storage of combustible materials in mechanical rooms is prohibited.

Improper Mechanical Room Storage

Storage Guidelines

- No storage is allowed in corridors and stairwells. A cluttered hallway could slow down emergency evacuation.
- Storage must not exceed a plane of 0.45 m below sprinkler heads or smoke detectors. Storage that breaks this plane may prevent sprinkler heads from fully covering room during a fire.



A staged example showing how storage can protrude into 0.45 m plane below sprinkler heads.

Myths about Sprinkler Systems

- **A sprinkler system will cause excessive water damage**
  - Sprinklers use a fraction of water compared with a fire hose.
  - Sprinklers release ~30 – 100 liters per minute compared to a fire hose at ~200 – 500 liters per minute.
  - Sprinklers operate very early in the fire development, and consequently require a smaller quantity of water.
- **When a fire occurs, every sprinkler head goes off**
  - Sprinkler heads are individually activated by fire.
  - > 50% of the fires are controlled by ≤ 4 sprinkler heads, and in many instances fires are controlled with one sprinkler.
- **The pipes burst due to freezing**
  - Sprinklers can be protected with various forms of frost protection, such as installing a dry system or providing heating elements to protect the sprinkler systems.

More Myths about Sprinkler Systems

- **Sprinkler systems might accidentally go off**
  - Sprinklers are very reliable; the chances of going off without mechanical assistance are 1 in 16 million; Fork lift truck drivers soon learn to avoid them.
- **Smoke detectors provide enough protection**
  - Smoke detectors provide early warning and save lives, but do nothing to extinguish a fire or protect those physically unable to escape on their own.
  - Too often, battery operated smoke detectors fail to function because the batteries are dead or have been removed.
- **Sprinklers are designed to protect property, but are not effective for life safety**
  - Sprinklers can reduce property losses up to 85%.
  - Combining sprinklers and early warning systems can reduce overall injuries, loss of life and property damage by 50%.

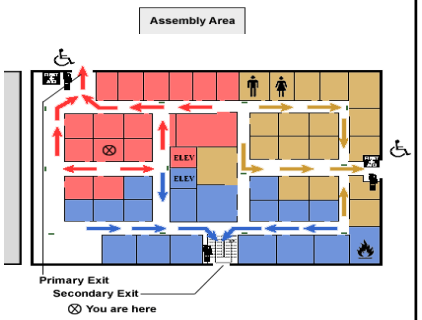
Fire Safety Planning

- **Construction**
  - Building materials
  - Fire-resistive ratings (minutes to hours)
  - Interior finishes (3 classes: A, B, & C)
- **Containing the fire**
  - Stair enclosures and fire walls
  - Separate building units or zones (control spread)
  - Fire doors
  - Smoke, heat and noxious gases control
  - Exits
- **Egress**
  - Two ways out, exit to safe area

Emergency Planning & Response

Have an evacuation plan for all buildings and areas and

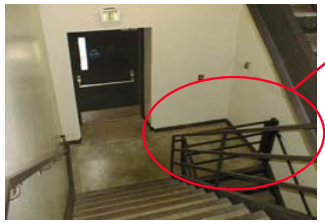
POST IT



Egress – Exit Route

- Exit routes must be permanent
  - Exits must be separated by fire-resistant materials
  - Openings into an exit must be protected by an approved self-closing fire door that **remains closed or automatically closes in an emergency**
  - Unobstructed
- Well marked

Best Practices: Safety During a Fire…



- Stairs have a bar blocking the steps going down to indicate ground level fire egress
- Keep fire exits and stairwells free from any obstruction to allow for an easy exit during a fire emergency

Emergency Lighting

Proper storage of Flammables is an important part of Fire Safety

Limit quantities stored

Safety cans

Secondary Containment

Flammable storage cabinets, rooms or buildings

Ventilation

Always provide adequate ventilation to reduce the potential for ignition of flammable vapors.

Storage Containers

- Oily Rags
- Drying process exothermic
- Container (reduces fire risk)
  - Limits oxygen.
  - Encourage air circulation to remove heat.
  - Limits access to ignition source.

Storage Containers

- **Containers should be tightly sealed when not in use.**
- **Approved safety cans are recommended for smaller quantities.**
  - The spring-loaded safety cap prevents spillage.
    - Prevents vapors from escaping
    - Acts as a pressure vent if engulfed in fire
    - Prevents explosions and rocketing of the can

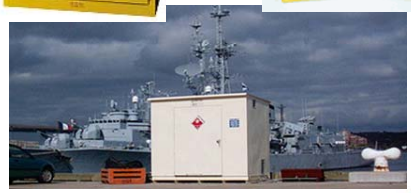
Flame Arrester Screen

- **Prevents fire flashback into can contents.**
- **Double wire - mesh construction**
- **Large surface area provides rapid dissipation of heat from fire so that vapor temperature inside can remains below ignition point.**

Storage Areas

Flammables should be stored in an approved cabinet in a cool, well ventilated area to avoid pressure buildup and vaporization

Flammable Storage Cabinets



Storage Cabinets

- Not more than 225 L of Class I and/or Class II liquids, or not more than 450 L of Class III liquids permitted in a cabinet.
- Must be conspicuously labeled, **“Flammable - Keep Fire Away”**
- Doors on metal cabinets must have a three-point lock (top, side, and bottom), and the door sill must be raised at least 5 cm above the bottom of the cabinet.

Static Electricity

- Some flammable liquids accumulate a static electric charge, which can release a spark that ignites the liquid
- Static electricity is generated by contact and separation of dissimilar materials:
  - **Fluid flow through a pipe or into a tank**
  - **Agitation or mixing**
  - **Splash filling of containers**

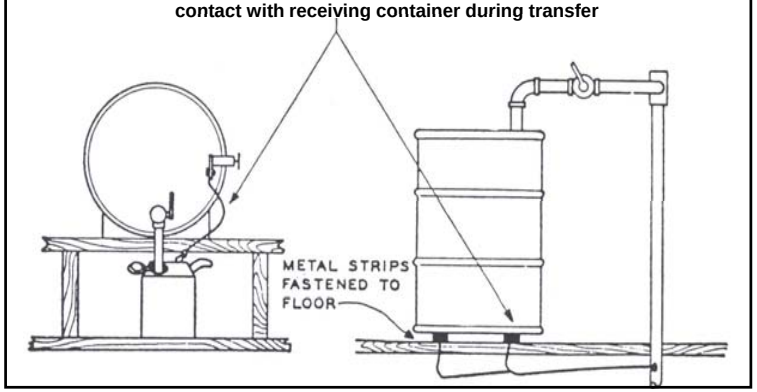
benzene toluene gasoline xylene

Transfer Techniques

- Bond containers
  - Containers are wired together before pouring
  - One container is connected to a good ground point to allow any charge to drain away safely
- Limit use of plastic containers to small volumes (< 4L)
  - No easy way to bond plastic containers

Control of Static

Bond wire necessary except where containers are inherently bonded together, or arrangement is such that fill stem is always in metallic contact with receiving container during transfer



Fire Prevention Inspections

- Minimize size of fires
  - Control storage of combustible and flammable materials
- Reduce possibility of a fire
  - Control ignition sources
- Ensure fire protection equipment is operational
  - Fire extinguishers not blocked
- Ensure exits are maintained
  - Don't block egress pathways
  - Don't prop open fire doors

Violations

Violations

6-Way Multi-plug

Multi-plug

Acknowledgement

Mercury Spill Cleanup,

University of Wisconsin Safety Office

http://www.uwm.edu/Dept/EHSRM/LAB/labHg.html

Questions?
Open Discussion