



Chemical
SAFETY AND SECURITY TRAINING

Chemical Safety and Security Officer Training

Bangkok, Thailand
14-18 February 2011



International Year of
CHEMISTRY
2011



SAND No. 2009-8395 P
Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company,
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under contract DE-AC04-94AL85000.



**Fire Extinguisher
Demonstration
and Practice**



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BREAK



3



**Chemical Toxicology and
Physiology**



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**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>



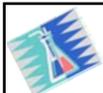
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Simplified Physiology



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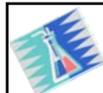
Major Parts of the Cell

**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



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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



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Routes of Exposure

Breathing Zone

Inhalation*

Absorption

Ingestion

Injection

Eyes

*Most important route of entry

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Respiratory System

Right lung

Upper lobe

Middle lobe

Lower lobe

Terminal bronchiole

Alveoli

Trachea

Left main bronchus

Tiny blood vessel (capillary)

Alveoli airspace

Red blood cell

The lungs contain millions of tiny alveoli

Oxygen (O₂) from air breathed in, goes into the red blood cells via alveoli. Carbon dioxide (CO₂) goes from the red blood cells into alveoli and breathed out.

Lung showing alveoli

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Conducting Passages

Upper respiratory tract

Nasal cavity

Pharynx

Larynx

Lower respiratory tract

Trachea

Primary bronchi

Lungs

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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 O₂
 - Open, clear airways.

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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 O₂ for CO₂ and exhale other gases/vapors.

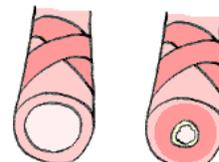


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Common Respiratory Issues

Chronic Bronchitis

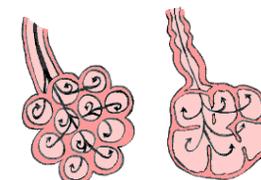


Normal Airway

Chronic Bronchitis

- Cells inflamed
- Airway narrow and clogged

Emphysema



Healthy Alveolus

Emphysema

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



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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



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Aerosol Penetration into the Lung

Size (micrometers)

> 20
10 – 20
5.0 – 10
0.1 – 5.0

% Deposition

100% in upper airways
80% upper, 0+ alveoli
50% upper, 50% alveoli
0+ upper, 90+ alveoli



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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 (COCl₂)
- Emphysema – smoke (esp. tobacco)
- Fibrosis – silicon dioxide (SiO₂)
- Cancer – asbestos (mesothelioma)



Asphyxiant / Suffocating Agent

- **Physical** – dilute oxygen in air to below 10%, non-irritant gases – methane, N₂, CO₂, Freon®
- **Chemical** – displace oxygen on hemoglobin – cyanide, carbon monoxide

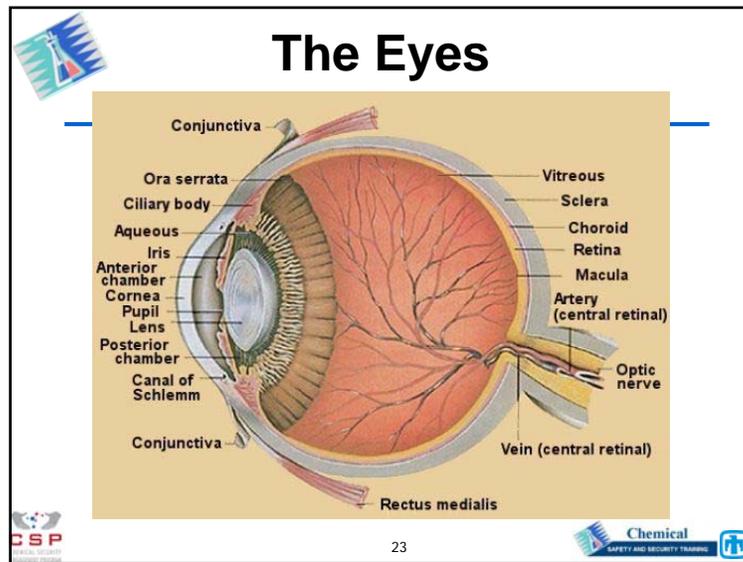
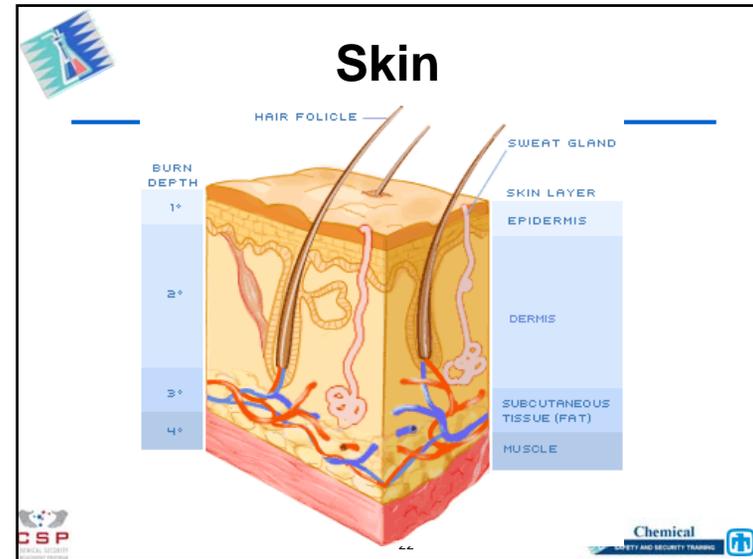
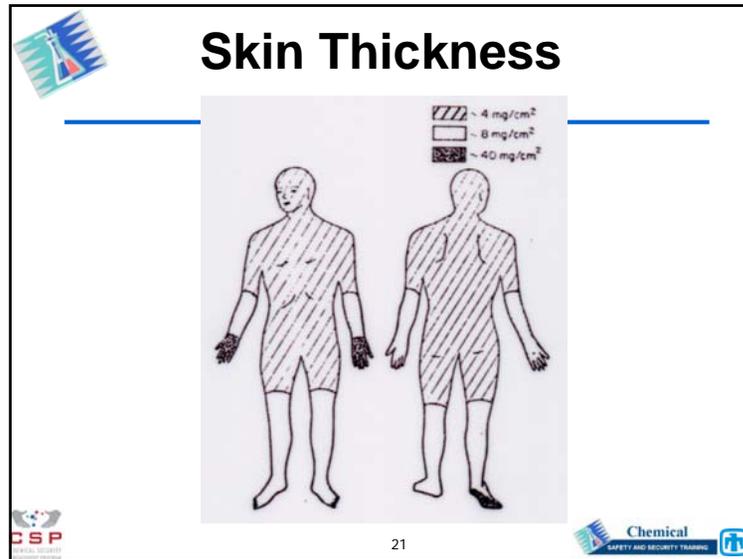


Routes of Exposure

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





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**



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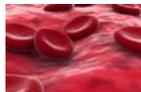
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Routes of Exposure

- **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 facilities)
 - especially hazardous in health care industry

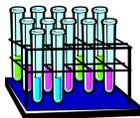


Chemical Toxicology



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

$$(\text{Toxicity}) \times (\text{Exposure}) = \text{Risk}$$



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

<u>Chemical</u>	<u>Beneficial Dose</u>	<u>Toxic Dose</u>
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

<u>Chemical</u>	<u>LD₅₀ (mg/kg)</u>
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)



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Factors Influencing Toxicity

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



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Toxicity Testing Assumptions

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



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Routes of Chemical Exposure

Occupational

- Inhalation
- Dermal/ocular
- Ingestion



Experimental

- Subcutaneous
- Gavage/ip/iv



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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

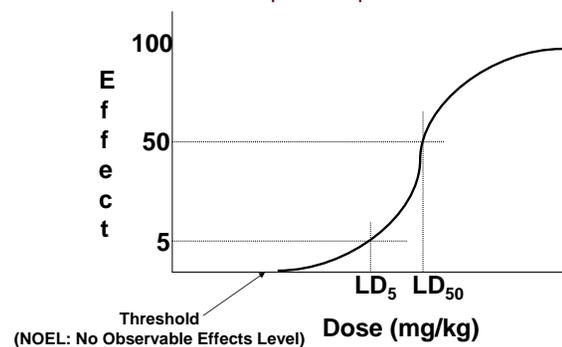
- With increasing dose, there is an increase in the number affected and/or an increase in the intensity of the effect: e.g., mortality; cancer; respiratory depression; liver pathology

$$\text{Dose} = (\text{Concentration}) \times (\text{Time})$$



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

- TD₁₀ – Toxic dose low - lowest dose for effect
- LD₁₀ – Lethal dose 10% - dose that causes death in 10% of the test population
- LD₅₀ – Lethal dose 50% - dose that causes death in 50% of the test population
- TC₁₀ – Toxic concentration low - used to express toxic concentration *via* inhalation
- LC₁₀ – Lethal concentration 10% - dose that causes death in 10% of the test population –*via* inhalation
- LC₅₀ – Lethal concentration 50% - concentration that causes death in 50% of the test population *via* inhalation



Concentration Units

Mass per Volume

- mg/m³ (milligrams per cubic meter)
- µg/m³ (micrograms per cubic meter)
- ng/m³ (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/m²)



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



<p>Benzene (C₆H₆) carcinogenic phenol, S-phenylmercapturic acid in urine</p>	<p>Xylene (C₆H₄(CH₃)₂) CNS, irritant methyl hippuric acid in urine</p>
<p>Toluene CNS depressant hippuric acid in urine</p> 	<p>Styrene dermatitis mandelic acid in urine</p> 
<p>Ethyl benzene irritant, dermatitis mandelic acid in urine</p> 	




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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)




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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)




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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
 - CCl₄ effects on the liver




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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).



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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)



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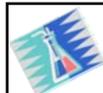
Target Organs

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)



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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	CONJUNCTIVITIS	ORGANIC SOLVENTS



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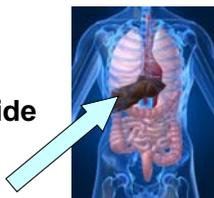




Target Organs

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 m²).

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) – H₂O₂
- Alopecia (loss of hair) - thallium



Target Organs

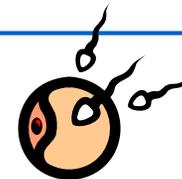
Reproductive and Developmental Disorders

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

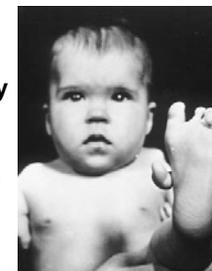


Teratogenicity

A specific type of developmental toxicity

Derived from Greek - monster formation

e.g., thalidomide



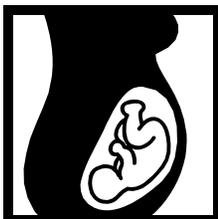
http://www.hemorctoday.com/images/hot/200904/aprila_thalidomide.jpg



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

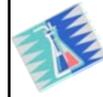




Toxic Effects of Some Specific Chemicals



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Metals



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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



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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



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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
2. 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 B₁₂
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



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Other Metals

H. Iron, Fe₂O₃

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)



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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)



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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



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Solvents and Vapors



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Halogenated Hydrocarbons

(low flammability, excellent solvents)

- Acute – CNS depression, defatting skin, myocardium
- Chronic – liver, kidney
- Chlorinated – solvents (CNS/skin/cancer)
CCl₄-carcinogenic, liver, kidney
- Brominated – fumigant, solvents (CNS/skin)
- Fluorinated – refrigerants (ozone layer/myocardium)



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Structure Affects Activity

- Useful, but dangerous – i.e., guilty by association, e.g., C₄F₈
- Branched chain isomer – lethal @ 0.5ppm
- Linear isomer – lethal @ 6,100ppm in 4 hr
- Cyclic isomer – essentially non-toxic



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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)



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Aliphatic Alcohols

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

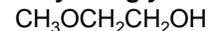


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Glycol Ethers

Ethylene glycol monomethyl ether (EGME)



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)



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

Propylene glycol monomethyl ether (PGME)

– Not a reproductive/developmental toxin



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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



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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



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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/m³) for solids
- Fibers per cubic centimeter (fibers/cc) for fibers

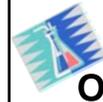
- **Absorbed Dose:**

Amount of substance deposited in or absorbed by an organism, expressed as:

- mg/kg



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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** – **Maximum Workplace Concentrations** – German, required legal limits.
- **BEI®** – **Biological Exposure Indices** – ACGIH, USA, recommendations.



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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.



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Action Levels and Policies

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



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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.

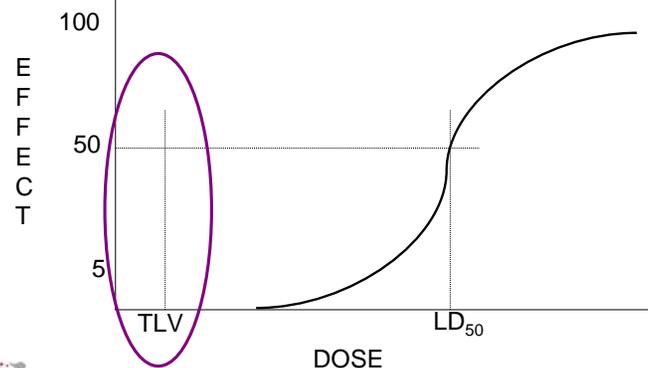
... may be affected more seriously by aggravation of a pre-existing condition or by development of an occupational illness.



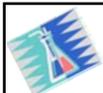
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Threshold Limit Values (TLV)



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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



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TLV Limitations

NOT

- **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.**



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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



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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



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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:

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

Where:

C = airborne concentration
T = time

* A TLV expressed as a TWA



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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:

$$\text{TLV-TWA}_8 = \frac{C_1T_1 + C_2T_2 + \dots + C_N T_N}{8 \text{ hrs}}$$



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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

$$\text{TLV-TWA}_8 = \frac{C_1 T_1 + C_2 T_2 + \dots + C_N T_N}{8 \text{ hrs}}$$

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

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

$$\text{TLV-TWA}_8 = \frac{C_1 T_1 + C_2 T_2 + \dots + C_N T_N}{8 \text{ hrs}}$$

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

EIGHT HOUR TLV-TWA = 75 ppm



Unit Concentration

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

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



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

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

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.

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



Mixtures

If the biological effects of mixture components are additive:

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

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



Acknowledgements

University of North Carolina
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Mary Carol Lewis,
NC Employment Security Commission, Raleigh NC USA



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Lunch



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Accident and Incident Investigation



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Reporting Chemical Incidents and Accidents



- All accidents, incidents, or suspicious occurrences should be reported to the supervisor, regardless of the perceived seriousness of the incident.
- Reporting helps indicate potential problem areas.
- Reports serve as a basis for corrective measures to prevent accidents/incidents from re-occurring with a more serious outcome.



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Serious Chemical Accidents and Incidents

- Should be reported in detail and should include:
 - Cause of accident/incident
 - Place, time, personnel involved
 - Diagram if necessary
 - Type of contamination or hazard
 - List of personnel possibly exposed
 - Decontamination procedures
 - Corrective actions taken
 - Medical attention taken (if appropriate)



Investigation and Prevention of Chemical Laboratory Accidents

- Emergency notification and response
- Written report of accident/incident
- Accident/Incident investigation response
- Review/investigation of accident/incident
- Determination of Cause
- Report and Implementation of Corrective Measures
- *Follow-up*



Accident/Incident Investigation Personnel

- Laboratory staff exposed or involved in accident/incident
- Laboratory Supervisor
- Safety/Security staff
- Medical personnel
- Administrative personnel
- Safety/Security Committee
- External experts, if needed



Written Accident/Incident Report

- A well written A/I Report provides quality information and data for investigation and remediation.
- Complete and accurate A/I information is critical to investigate the circumstances and to help prevent against future A/I occurrences.



Accident/Incidence Investigation Response

- Have a written procedure to submit A/I reports
- Include:
 - Procedure to form an *ad hoc* A/I Safety/Security Investigation Team for each A/I with designation of special A/I investigation team members if necessary (e.g., biological, radiation).
 - Specify an odd number of Investigation team members.
 - Specify that CSSO or organization SO is secretary but *ex-officio* (non-voting) member of Investigation Team.
 - Designate time required for A/I Investigation Team members to review and respond (by e-mail, if possible) on A/I Report.
 - Time required for Safety/Security Committee to determine if an A/I Investigation is necessary, when it is to be conducted, and who should be on Team.
 - Time required for Investigation Team and Safety/Security Committee to issue written investigation report, who the report goes to and that it contain corrective recommendations to help assure A/I will not reoccur, if appropriate.



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Review/Investigation of Accident/Incident

- Site investigations and interviews can be the center of an A/I investigation program
- An A/I analysis and corrective actions can be determined from the data and information provided during this phase
- The data quality is important and a uniform approach to conducting the investigation is essential
- It is important in this step to obtaining and verify relevant personal and facility information
- The data may include testing, evaluation or verification of records for safety procedures, training, reporting, regulations, documentation and equipment
- The use of interviews of injured persons and witnesses can be very important to obtain all the facts



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Determination of Cause

- An analysis of the A/I is performed using the information collected during the site investigation and interviews
- The analysis determines the cause of an A/I and tracks it back to the cause
- The object is to reveal the causes of the A/I and to understand what happened, how, when and why it occurred



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Report and Implementation of Corrective Measures

- After the investigation and interviews, Team members meet to draft an Investigative report .
- An objective written report is issued that summarizes the feeling of the Team members that includes effective corrective measures to be implemented to prevent or minimize similar future accidents/incidents.
- The Team's recommended corrective actions should include:
 - The extent of the measures (i.e., specific to a laboratory or wider).
 - Resources needed for implementation.
 - Expected outcome.
- The Team's Report should be sent to all individuals involved in the A/I as well as the Laboratory Supervisor, Administration, and Institute Higher Management, External Government Agencies, if appropriate.



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Accident/Incident Follow-up

- The corrective measures recommended by the Investigation team should be monitored to insure they implemented properly and have the desired effect
- Recommended actions should include a timeframe for completion

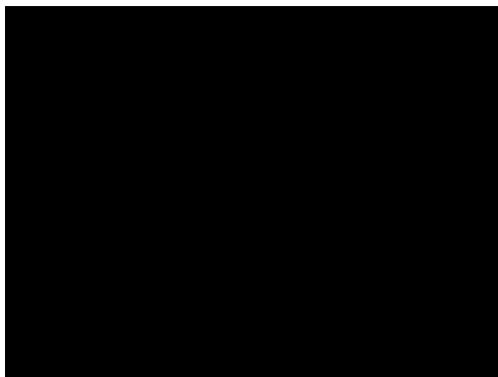


Accident/Incident Follow-up Timeline

- Length of timeline depends on nature and severity of incident.
- Starts at time/date of accident or incident.
- Incident should be reported immediately to:
 - CSSO, PI, Security Office, and/or Medical Office
 - Management or administration. Depends on incident severity, but usually with 2 days.
- Investigation usually starts within 24 hours.
- Written report is issued within a week.
- Report should include time for recommended follow-up actions, usually days to months.



CSB Video –Incident Investigation Example



Safe/Secure Transport of Chemicals



Transport References

UNECE, "Globally Harmonized System Of Classification and Labeling of Chemicals (GHS)," 1st edition, 2003, online, http://www.unece.org/trans/danger/publi/ghs/ghs_rev00/00files_e.html

International Airlines Transportation Association, Dangerous Goods Regulations(DGR), 2008, not online,

<http://www.iata.org/ps/publications/9065.htm>

UN International Maritime Organization (IMO),

<http://www.imo.org/>

European Union (EU) Transport Activities

<http://europa.eu/>

US Department of Transportation (DOT)

<http://www.dot.gov>



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International Shipping Fines

- For international shipments fines are severe
 - up \$250,000 fine + 5 years prison in US
- Apply to scientists improperly transporting
 - samples
 - test material
 - specimens
- Dangerous Goods Regulations are set by:
 - IATA: International Air Transport Association



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Modes of transport



- Air
- Ship
- Rail
- Road



- Vehicle (car/truck)
- Cart, Bicycle
- Hand carry



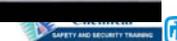
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Always expect the unexpected



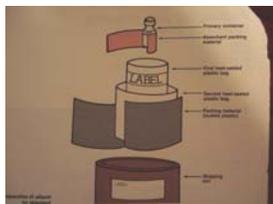
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Universal Safety/Security Concept

Container within a Container



What is a hazardous chemical shipment?

- Corrosives
- Dry ice
- Explosives
- Flammables
- Gases
- Flammable liquids
- Flammable solids
- Genetically modified organisms
- Infectious substances
- Magnetized material
- Oxidizing substances
- Radioactive substances
- Toxic substances
- Aerosols



Are there special shipping requirements?

What are the physical and chemical properties?



dry ice, refrigeration?

Are specific containers required?
size, strength, composition



Specific transport concerns

- Quantities, exclusions, limitations
- Restricted routes:
tunnels
bridges
populated areas





Sender/Shipper Should Know

- Who transports the material?
- How is it transported?
- How is it packaged?
- Are transporters knowledgeable and prepared?
- Is there safety documentation?
- When did it leave, arrival time?
- Did all material depart and arrive as scheduled?



Labels continued



properly and fully identify material

use proper, full chemical name
no abbreviations
ID codes, e.g., UN Numbers

specify
quantities, concentrations,
number of containers



Labels continued



indicate specific hazard class
according to regulations

include
emergency information
contact names
24/7 phone numbers



language(s)
proper universal symbols



Documentation



shipping order
bill of lading
manifest

full shipper, receiver addresses
packing & labeling certification
verification of receipt





Documentation continued



Safety Data Sheets

follow up documentation
require incident/accident
reports



Handling

- Where, how, who opens shipment?
- Should package be opened in a hood?
- Is material radioactive?
- Is monitoring equipment needed?
- Is special storage needed on receipt?



Who requires training?

- Managers
- Packers
- Handlers
- Loaders
- Drivers
- All shipping and receiving personnel
- Mailroom personnel



Emergency Preparation

- Transportation accidents/incidents:
 - Organization reports
 - Police reports
 - Emergency contacts
- Spill and leakage control:
 - prevention
 - minimization
 - spill clean up kits
 - PPE
- Emergency contacts
 - Regulation requirements
 - local, national, international





Emergency preparation continued

- Emergency contacts
 - Regulation requirements
 - local, national, international
- Public relations
 - Designate spokesperson beforehand
 - Be responsive to public concerns



Plan ahead

- Have a plan
- Remember:
 - Anticipation
 - Recognition
 - Evaluation
 - Control



Safety equipment should have a routine check.



Unsafe Transport of Gas Cylinders



Acknowledgement

International Labour Organization (ILO)

International Occupational Safety and Health Centre (CIS)

Programme on Safety and Health at Work and the Environment (SafeWork)

<http://www.ilo.org/public/english/protection/safework/cis/index.htm>



Any Questions?



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BREAK

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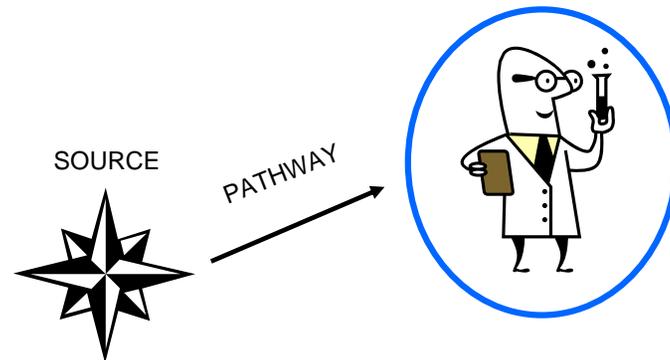


Personal Protective Equipment (PPE) and Safety Equipment Performance Specifications

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Worker Protection



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Personal Protective Equipment (PPE)

- **Should be a last resort, but may be necessary if:**
 - engineering controls inadequate or being installed
 - administrative controls don't do the job
 - emergency response or spill cleanup
 - supplement other control techniques if can't achieve required level
- **Depends upon human behavior**
 - proper selection, fit and comfort issues
- **Hazard is still present with PPE ...**



US/OSHA PPE Regulations

- **Eye and face protection**
 - 29 CFR 1910.133
- **Respiratory protection**
 - 29 CFR 1910.134
- **Head protection**
 - 29 CFR 1910.135
- **Foot protection**
 - 29 CFR 1910.136
- **Hand protection**
 - 29 CFR 1910.138
- **Hearing Protection**
 - 29 CFR 1910.95



www.cdc.gov/nasd/menu/topic/ppe.html
www.osha.gov/SLTC/personalprotectiveequipment/index.html
www.osha.gov/Publications/OSHA3151.pdf



Training and Qualification

Employees should be trained to know:

- When PPE is necessary?
- What PPE is necessary?
- How to properly don, doff, adjust and wear PPE.
- Limitations of PPE.
- Proper care, storage, maintenance, useful life, and disposal of PPE.



www.free-training.com/osha/ppe/ppemenu.htm



Training and Qualification

Retraining is necessary when there is:

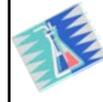
- Change in the process.
- Change in type of PPE used.
- Inadequate employee knowledge or use of PPE.
 - retrain to reinforce understanding or skill





Personal Protective Clothing (PPE)

- Evaluate task, select appropriate type and train to use it properly
 - lab coats, gowns, aprons
 - safety glasses (with side shields), goggles, face shields
 - gloves
- Remove PPE before leaving the lab



Protective Equipment Works

"It's a hot day, why wear a lab coat?"



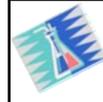
An experiment reacted unexpectedly and a flammable solvent from a hood splashed out and landed on the bottom of the lab coat



Eye and Face Protection



- Thousands are blinded each year from work-related eye injuries.
- Nearly *three out of five* workers are injured while failing to wear eye and face protection.



Eye & Face Protection



- Safety glasses
- Goggles
- Face shield





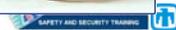
Eye and Face Protection

Eye protection shields eyes by:

- Primary protection:
 - Safety glasses with side shields protect from flying objects.
 - Goggles prevent objects from entering under or around the eyewear.
- Secondary protection:
 - Face shields
 - Combine with safety glasses or goggles
 - Do not protect from impact hazards



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Hazard Assessment

Hazard Type	Hazard Type	Common related tasks
Impact	Flying objects such as large chips, fragments, particles, sand, and dirt	Chipping, grinding, machining, masonry work, wood working, sawing, drilling, riveting, sanding,...
Heat	Anything emitting extreme heat	Furnace operations, pouring, casting, hot dipping, welding, ...
Chemicals	Splash, fumes, vapors, and irritating mists	Acid and chemical handling, degreasing, plating, and working with blood or OPIMs
Dust	Harmful dust	Woodworking, buffing, and general dusty conditions
Optical Radiation	Radiant energy, glare, and intense light	Welding, torch-cutting, brazing, soldering, and laser work



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Biohazards

Use caution *anytime* you are working with blood or other bodily fluids.

Contaminated blood or bodily fluids may result in transmission through the eyes.



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Eye and Face Protection

Optical Hazards

- Welding helmets are secondary protection to shield from UV, heat, and impact.
- Exposure to laser beams requires suitable laser safety goggles with protection for the *specific wavelength*.



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Eye and Face Protection Requirements

- Eye and face protection should comply with the American National Standards Institute:
 - ANSI Z87.1-1989
- Ensure employees who wear prescription lenses or contact lenses:
 - Use safety eyewear that incorporates the prescription
 - Use eye protection that can be worn over prescription lenses



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Additional Considerations

- Provide adequate protection against the specific hazards.
- Safe design and construction for the work to be performed.
- Comfortable.
- Don't interfere with the wearer's movements.
- Durable!
- Capable of being disinfected.
- Easily cleaned.
- Distinctly marked to indicate they are approved eye protection.
- Worker satisfaction.
 - – Include workers in the selection process.



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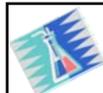


Eyewash and Showers

- US regulations
 - 29 CFR 1910.151(c)
 - ANSI Z358.1-2004
- Types
 - eyewash
 - shower
 - drench hose
- Concerns
 - drainage
 - freezing
 - contaminated water



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Eyewash and Showers

- Know their locations
- Maintenance and testing program
- Concerns:
 - drainage
 - freezing
 - contaminated water



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Eyewash Standards



- Eye wash stations
 - Minimum 0.4 to 3.5 gal/min (1.4 – 13.2 l/min.)
 - Flush for 15 minutes
- Provide flow for both eyes
 - Hold eyes open
 - Tepid, pH match eye (preferred)
- Easily accessible locations
 - 33 to 45 in. (84-114 cm) from floor
 - 6 in. (15cm) from wall
- Test weekly
 - Portable: clean/refill (6 mo – 2 yrs)
- Various types

ANSI Z358.1

NC DOL Guide:

www.nclabor.com/osha/etta/indguide/ig28.pdf

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Safety Shower Standards

- Within 55 ft. (17 m) or 10 seconds
 - Normal walking = 3.8 mph (6.1 km/hr)
- Test monthly
- Pull within reach (highly visible)
 - 82 to 96 in. high (208 – 244 cm)
 - Deliver 20 in (51 cm) column
 - Height: 60" (152 cm) above floor
- 20–30 gal/min (76-114 L/min)
- Tepid: 60 to 100 °F (16 – 38°C)



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Safety Shower Standards cont.

Consider:

- Drains
- Blankets/modesty curtains

Avoid or protect electrical outlets

- ANSI Z358.1-2004



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Blocked Eyewash & Safety Shower



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Dirty Eyewash Station



Blocked Eye Wash Station



Hand Protection

- **Glove considerations**
 - Type glove
 - Dexterity required
 - Chemical & physical
 - material
 - strength
 - Exposure time
 - breakthrough time
 - Size, comfort, reusable/disposable
- Manufacturer selection charts



Glove Selection

- **Considerations:**
 - Chemicals (splashes vs immersion)
 - Thermal (extreme heat/cold)
 - Abrasion; cuts; snags; splinters; punctures
 - Grip: oily, wet, dry
 - Comfort, fit, size
 - Ergonomics





Chemical Protective Gloves/ Clothing

- **Permeation (“silent killer”)**
 - Substances pass through intact material on a molecular level.
- **Penetration**
 - Substances pass through seams, zippers, stitches, pinholes, or damaged material.
- **Degradation**
 - Substance damages material making it less resist or resulting in physical breakdown.
- **Contamination**
 - Substances transferred inside material (improper doffing or decontamination).



Permeation Rate (PR)	Permeation Breakthrough (PB)	Permeation Degradation rate (DR)
E - Excellent; permeation rate of less than 0.9 mg/cm ² /min	>Greater than (time - minutes)	E - Excellent; fluid has very little degrading effect.
VG - Very Good; permeation rate of less than 9 mg/cm ² /min	< Less than (time - minutes)	G - Good; fluid has minor degrading effect.
G - Good; permeation rate of less than 90 mg/cm ² /min		F - Fair; fluid has moderate degrading effect.
F - Fair; permeation rate of less than 900 mg/cm ² /min		P - Poor; fluid has pronounced degrading effect.
P - Poor; permeation rate of less than 9000 mg/cm ² /min		NR - Fluid is not recommended with this material.
NR - Not recommended; permeation rate greater than 9000 mg/cm ² /min		† Not tested, but breakthrough time > 480 min DR expected to be Good to Excellent
		†† Not tested, but expected to be Good to Excellent based on similar tested materials



Gloves



- It's important to have the *right glove* for the job and know *how long* it will last.
- **Glove Chart Examples:**
 - Consider several glove manufactures data before final selection.
 - www.bestglove.com/site/chemrest/

The first square in each column for each glove type is color coded. This is an easy-to-read indication of how we rate this type of glove in relation to its applicability for each chemical listed. The color represents an overall rating for both degradation and permeation. The letter in each square is for Degradation alone...

GREEN: The glove is very well suited for application with that chemical.
 YELLOW: The glove is suitable for that application under careful control of its use.
 RED: Avoid use of the glove with this chemical.

CHEMICAL	LAMINATE FILM		NITRILE		UNSUPPORTED NEOPRENE		SUPPORTED POLYVINYL ALCOHOL		POLYVINYL CHLORIDE (Vinyl)		NATURAL RUBBER		NEOPRENE/NATURAL RUBBER BLEND	
	BARRIER		SOL-VEX		29-865		PVA		SNORKEL		CANNERS AND HANDLERS*		CHEMI-PRO*	
	Degradation Rating	Permeation Breakthrough (mg/cm ² /min)	Degradation Rating	Permeation Breakthrough (mg/cm ² /min)	Degradation Rating	Permeation Breakthrough (mg/cm ² /min)	Degradation Rating	Permeation Breakthrough (mg/cm ² /min)	Degradation Rating	Permeation Breakthrough (mg/cm ² /min)	Degradation Rating	Permeation Breakthrough (mg/cm ² /min)	Degradation Rating	Permeation Breakthrough (mg/cm ² /min)
1. Acetaldehyde	■	380	E	—	—	E	10	F	■	—	—	E	7	F
2. Acetic Acid	■	150	—	G	270	—	E	60	—	—	F	180	—	E
3. Acetone	▲	>480	E	—	—	E	10	F	—	—	—	E	10	F
4. Acetonitrile	▲	>480	E	F	30	F	E	20	G	■	150	G	—	—
5. Acrylic Acid	—	—	—	G	120	—	E	300	—	—	—	E	80	—
6. Acrylonitrile	E	>480	E	—	—	—	—	—	—	—	—	—	—	—
7. Allyl Alcohol	▲	>480	E	F	140	F	E	140	VG	—	—	—	—	—
8. Ammonia Gas	—	19	E	▲	>480	—	▲	>480	—	—	—	■	6	VG
9. Ammonium Hydroxide, 40%	—	—	—	E	>360	—	E	>480	—	—	E	>360	—	E
10. Anomium Hydroxide	E	30	—	E	>360	—	E	250	—	—	E	240	—	E
11. Amyl Acetate	▲	>480	E	E	60	G	—	—	—	—	—	—	—	—
12. Amyl Alcohol	—	—	—	E	30	E	E	290	VG	G	180	G	G	12
13. Aniline	▲	>480	E	■	—	—	E	100	P	F	>360	E	F	180
14. Aqua Regia	—	—	—	F	>360	G	>480	—	—	—	G	120	—	—
15. Benzaldehyde	▲	>480	E	■	—	—	—	G	>360	E	—	—	G	10
16. Benzene, Benzol	▲	>480	E	■	—	—	—	E	>360	E	—	—	—	—
17. Benzotrifluoride	—	—	—	E	>480	E	—	—	—	—	—	—	—	—
18. Benzotrifluoride	—	—	—	E	170	G	F	—	E	—	G	>10	F	50
19. Bromine Water	—	—	—	E	>480	E	E	>480	E	—	—	—	—	—
20. 1-Bromopropane	▲	>480	F	■	23	F	■	>10	P	▲	>480	E	■	>10



Types of Gloves

Polyethylene/Ethylene-vinyl Alcohol {"Silver Shield®"}

- Resists permeation and breakthrough with chemicals.
- Uses: aromatics, esters, ketones, and chlorines.



Butyl

- Highest permeation resistance to gas or water vapors.
- Uses: ketones (MEK, acetone) and esters (amyl acetate, ethyl acetate).



Types of Gloves

Viton®

- Highly resistant to permeation by chlorinated and aromatic solvents
- Can be used with water/water based solvents



Nitrile (acrylonitrile-butadiene rubber)

- Good replacement for latex
- Protects against acids, bases, oils, aliphatic hydrocarbon solvents and esters, grease, fats
- Resists cuts, snags, punctures and abrasions



Types of Gloves

Neoprene

- Protects against acids, caustics, DMSO.
- Resists amines, alcohols, glycols.
- Limited use for aldehydes and ketones.

Poly vinyl chloride (PVC)

- Protects against acids, caustics.
- Resists alcohols, glycols.
- Not useful for aromatics, aldehydes and ketones.



What is latex allergy?

- Natural rubber latex is from the rubber tree *Hevea brasiliensis*.
- The major route of occupational exposure is absorption of latex protein through the skin.
- Allergens in or on gloves can be transferred to the person's tissue.





Latex Allergies

- Symptoms may occur within minutes of exposure or may take several hours depending on the individual.
 - Skin Redness
 - Hives
 - Itching
 - Respiratory Symptoms
 - Runny Nose
 - Itchy Eyes
 - Scratchy Throat
 - Asthma



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Latex Allergy



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Latex Allergies

- To prevent latex allergies consider:
 - Using non-latex gloves.
 - If you choose latex gloves, use the powder-free version.
 - When using gloves, do not use oil-based hand cream or lotions (these cause glove deterioration).
 - Recognize the symptoms of latex allergy.
 - Always wash hands after removing gloves.

<http://www.cdc.gov/niosh/topics/latex/>
<http://www.nursingworld.org/osh/latex.htm>



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Proper Steps for Removing Gloves



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Respiratory Protection Program

- Written program
- Administered by Safety Office
- Medical clearance
 - Respiratory Protection Questionnaire
 - No beards
- Fit testing
- Respirator selection
 - Air monitoring
- Training (annual refresher)



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Respiratory Protection Standards

- 29 CFR 1910.134
 - OSHA Respiratory Protection Standard
 - New OSHA Assigned Protection Factors
- ANSI Z88.2–1992
 - ANSI Voluntary Consensus Standard



Conduct an Exposure Assessment:

www.osha.gov/SLTC/etools/respiratory/haz_expose/haz_expose.html

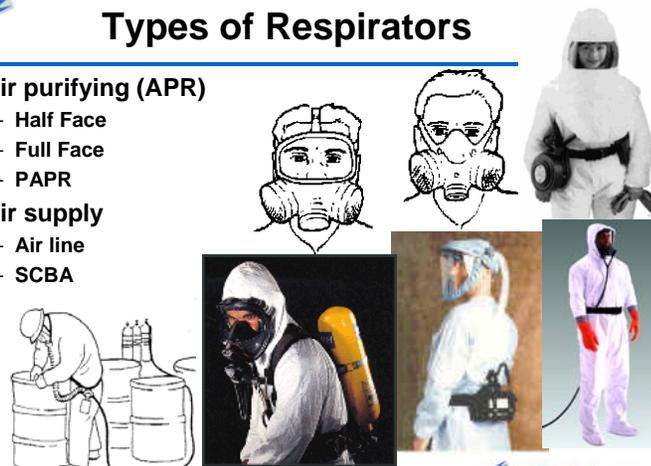


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Types of Respirators

- Air purifying (APR)
 - Half Face
 - Full Face
 - PAPR
- Air supply
 - Air line
 - SCBA



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Air Purifying Respirators

- **Must have at least 19.5% oxygen.**
 - Never use in O₂ deficient atmospheres
- **Only filters the air.**
 - Particulate filters
 - Removes aerosols
 - Chemical cartridges or canisters
 - Remove gases and vapors
- **Concentrations must not exceed limitations of filter/cartridge.**
- **PAPR (Powered Air Purifying Respirator)**
 - Uses a blower to force air through an air purifying element



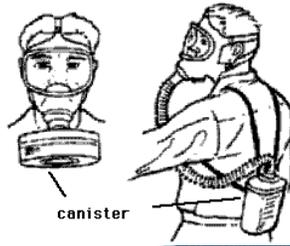
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APR Chemical Cartridge Selection

- Specific gases or vapors
- NIOSH or MSHA approval
- Adequate warning properties
- End of service life
- Mechanisms
 - adsorption
 - absorption
 - chemical reaction
- Breakthrough times
- *Proper maintenance and storage*



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Cartridge Selection

Cartridge	Description
	Organic Vapor
	Organic Vapor and acid gases
	Ammonia, methylamine and P100 any particulates filter 99.97% minimum filter efficiency



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End of Service Life Indicators (ESLI)

There are very few NIOSH-approved ESLI's:

- ammonia
- carbon monoxide
- ethylene oxide
- hydrogen chloride
- hydrogen fluoride
- hydrogen sulfide
- mercury
- sulfur dioxide
- toluene-2,4-diisocyanate
- vinyl chloride



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Assigned Protection Factors (APF)

- Level of workplace respiratory protection that a respirator or class of respirators is expected to provide.
- Each specific *type* of respirator has an Assigned Protection Factor (APF).
- Select respirator based on the exposure limit of a contaminant and the level in the workplace.

$$\text{Maximum Use Concentration (MUC)} = \text{APF} \times \text{Occupational Exposure Limit (e.g. OEL, TLV)}$$



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Assigned Protection Factors

Type of Respirator	Half Face Mask	Full Facepiece	Helmet/Hood	Loose-Fitting Facepiece
Air-Purifying	10	50	-	-
PAPR	50	1,000	25/1,000	25
Supplied-Air or Airline				
- Demand	10	50	-	-
- Continuous flow	50	1,000	25/1000	25
- Pressure demand	50	1,000	-	-
SCBA				
- Demand	10	50	50	-
- Pressure Demand	-	10,000	10,000	-



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Assigned Protection Factors

Workplace air sampling indicates the exposure to benzene is 30 ppm. OEL is 1 ppm. What respirator should you choose?

Maximum Use Concentration (MUC) = OEL x APF

Half Face Mask: MUC = 1 ppm x 10 = 10 ppm

PAPR (LFF): MUC = 1 ppm x 25 = 25 ppm

Full Face Respirator: MUC = 1 ppm x 50 = 50 ppm



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Dust Masks vs. Hospital Masks



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High Efficiency Particulate Air Filter (HEPA) Respirator



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Fit Testing

- **Qualitative**
 - Irritant smoke (stannic chloride)
 - Isoamyl acetate (banana oil)
 - Saccharin
 - Bitrex (bitter taste)
 - *Employees should perform a user seal check each time they put on a tight-fitting respirator*
- **Quantitative**
 - Portacount



Qualitative Fit Test

Pass/Fail Fit Test

- Assess the adequacy of respirator fit
- Relies on the individual's response to a test agent



Qualitative Fit Test

Positive / Negative pressure fit test



Supplied Air

- Supplies breathing air to employee
- **Examples:**
 - SCBA
 - Airline
- **Grade D Air**
- **Limitations**





Breathing Air Quality and Use

- **Compressed breathing air must be at least Type 1 - Grade D [ANSI/CGA G-7.1-1989]:**
 - Oxygen content = 19.5 - 23.5%
 - Hydrocarbon (condensed) = 5 mg/m³ or less
 - CO ≤ 10 ppm or less
 - CO₂ of 1,000 ppm or less
 - Lack of noticeable odor
- **Compressors equipped with in-line air-purifying sorbent beds and filters.**



Breathing Air Quality and Use

- **Non-oil lubricated compressors**
 - CO levels in the breathing air ≤ 10 ppm
- **Oil-lubricated compressors**
 - High-temperature or CO alarm, or both
 - If only high-temperature alarm, the air supply must be monitored to prevent CO levels from exceeding 10 ppm



Maintenance and Storage Procedures

- **Disposable filtering face-piece:**
 - Dispose after use
- **Half-mask:**
 - Write expiration date (current date + estimate) making sure to keep entire label legible
 - Discard cartridges based on expiration date, end-of-service life indicator or calculated service life
 - Clean
 - Dry
 - Place in sealable bag (write your name on bag)
 - Contact Safety Office for repairs



Maintenance and Storage Procedures

- **Exclusive use of an employee:**
 - Clean and disinfect as often as necessary to be maintained in a sanitary condition.
 - Discard cartridges based on expiration date, end-of-service life indicator or calculated service life.
- **Respirators issued to more than one employee or maintained for emergency use:**
 - Clean and disinfect before worn by different individuals or after each use.
- **Respirators used in fit testing and training:**
 - Clean and disinfect after each use
- **All respirators *must* be stored in clean, dry bags**



Hazards Requiring Body Protection

- *Hazardous chemicals.*
- Potentially infectious materials.
- Intense heat.
- Splashes of hot metals and hot liquids.



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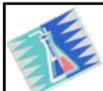
Body Protection for Emergency Response

Full suits:

- Class A
- Class B
- Class C
- Class D



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Level A Protective Suits

Potential exposure to unknown:

- Greatest level of skin, respiratory, and eye protection.
- Positive-pressure, full face-piece Self Contained Breathing Apparatus (SCBA) or positive pressure supplied air respirator with escape SCBA.
- Totally encapsulated (air-tight) chemical and vapor protective suit.
- Inner and outer chemical-resistant gloves, and boots.



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Level B Protective Suits

- Atmospheric vapors or gas levels not sufficient to warrant level A protection.
- Highest level of respiratory protection, with lesser level of skin protection.
 - Positive-pressure, full face-piece self contained breathing apparatus (SCBA) or positive pressure supplied air respirator with escape SCBA
 - Hooded chemical resistant clothing or coveralls (non-totally-encapsulating suit), inner and outer chemical-resistant gloves, and boots



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Level C Protective Suits

- Concentration or contaminant known
- Full-face air purifying respirator permitted with a lesser skin protection_
- Inner and outer chemical-resistant gloves, hard hat, escape mask, disposable chemical-resistant outer boots
 - *Difference in Level C and level B is respiratory protection*



Level D Protective Suits

- Minimum protection.
- *No* respiratory or skin protection.
- Used only if no known or suspected airborne contaminants present.
- May include gloves, coveralls, safety glasses, face shield, and chemical-resistant, steel-toe boots or shoes.



Foot Protection

Should meet or exceed ANSI Standard.

Types:

- Impact, penetration, compression, steel toe, etc.
- Non-skid, with slip resistant soles.
- Chemical resistant (rubber, vinyl, plastic, with synthetic stitching to resist chemical penetration).
- Anti-static
- Temperature resistant (high or low extremes).
- Electrical protection (non-conducting).
- Water resistant
- Combination shoes



Personal Protective Equipment Foot Protection

Steel toe-safety shoes are not necessary for laboratory work *unless* there is a serious risk from transporting or handling heavy objects.



However,
open toe shoes
should NOT be worn in labs.



Head Protection



Should meet or exceed Z89.1-2003

Types:

- Bump caps - don't meet ANSI standard, provide minor protection
- Electrical protection 2200-22,000 v, depends on class)
- Mining protection
- Classic-- high impact general purpose protection.
- Impact 850-1000 pounds (386 - 454Kg)
- Penetration 3/8" (~1cm)



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Any Questions?



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Questions?
Open Discussion
Homework



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