Chemical
SAFETY AND SECURITY TRAINING

Chemical Safety and Security Workshop

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Sandia National Laboratories

Chemical Management Best Practices

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Environmental & Chemical Safety Educational Institute

Chemical SAFETY AND SECURITY TRAINING

Chemical and Waste Management

Best Practices

References

"Less is Better," American Chemical Society, Washington DC, 2003, available online: http://membership.acs.org/c/ccs/publications.htm

"School Chemistry Laboratory Safety Guide," US NIOSH Publication 2007-107, Cincinnati, OH, 2006, available on-line: http://www.cpsc.gov/CPSCPUB/PUBS/NIOSH2007107.pdf

"Prudent Practices in the Laboratory: Handling and Disposal of Chemicals," National Academy Press, 1995, available online: http://www.nap.edu/catalog.php?record_id=4911

Chemical Management

Institute a Safety Program

- Have a Safety Manual
- Appoint a chemical safety officer for each major area/section/group/building
- Form a Safety Committee
- Have periodic safety training (films, etc)
- Have safety inspections
- Investigate serious accidents/incidents
- Follow-up!

Cradle - to - grave care of chemicals

Receipt → **Storage** →

Use → **Disposal**

Plan experiments in advance!

What chemicals are needed?

How much is needed?

How will the chemicals be handled?

What are the reaction products?

How will the chemical be stored?

How will disposal take place?

Inventory management

Less is Better !

- **Order only what you need**
- **Reduce size of experiment**
  - **It cost less to store**
  - **It cost less to dispose**

"Less is Better: Guide to minimizing waste in laboratories", Task Force on Laboratory Environment, Health and Safety, American Chemical Society, 2002. http://membership.acs.org/C/CCS/pub_9.htm

Inventory management

Less is Better !

It's Safer!

It may be cheaper to order diethyl ether in large containers

But, if it's opened for a long time—peroxides can form!

Inventory management

-R-O-O-R-

Peroxide Forming Chemicals

Even with inhibitors they can become dangerous over time

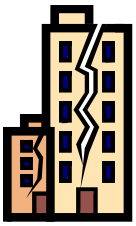
Examples: ethers, dioxane, tetrahydrofuran

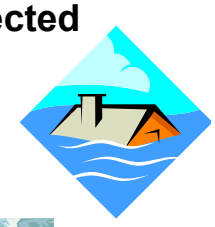
- **discard or test if unsure**
- **label & date when received, when opened, and provide expiration date**

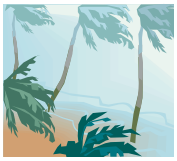
References: See for example, http://www.med.cornell.edu/ehs/updates/peroxide_formers.htm

Chemical storage

- Protect chemicals during normal operations
- Protect chemicals during unexpected events
  - Floods
  - Tidal waves
  - Earthquakes
  - Typhoons
  - Hurricanes







Chemical storage: Basic concepts

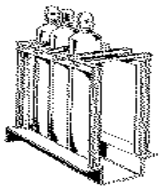
- Separate incompatible chemicals
- Separate flammables/explosives from ignition sources
- Use flammable storage cabinets for large quantities of flammable solvents
- Separate alkali metals from water
- Separate acids and bases

Use flammables storage cabinets

Chemical storage: Basic concepts

- Store nitric acid separately
- Store large containers on bottom shelves
- Lock up drugs, chemical surety agents, highly toxic chemicals
- Do not store food in refrigerators with chemicals

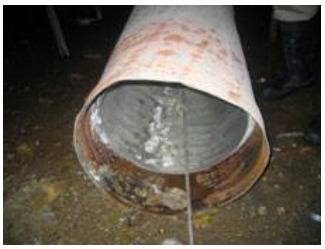
Chemical storage: Gas cylinders



- Secure (chain/clamp) and separate gas cylinders
- Screw down cylinder caps
- Store in well-ventilated area
- Separate & label empty cylinders
- Store empty cylinders separately
- Separate flammable from reactive/oxidizing gases

Improper gas cylinder storage/handling

Gas Cylinders



Exploded nitrogen cylinder

Chemical storage: Cryogenics

- Store gases & cryogenics separately from other chemicals
- Store cryogenics (liquid nitrogen) & dry ice in well ventilated areas
- Use proper PPE (including eye protection) when handling & moving cryogenics
- Do not use cryogenics in closed areas

Chemical storage: Good practices

- Limit access
  - Label "Authorized Personnel Only"
  - Lock area/room/cabinets when not in use
- Be sure area is cool and well ventilated
- Secure storage shelves to wall or floor
- Shelves should have a ¾" front lip
  - In earthquake territory, have a rod several inches above shelf

- Separate incompatible chemicals
  - Organize chemicals by compatible groups
  - Alphabetize chemicals only within compatible groups

Chemical storage: Bad practices

- Do Not Store Chemicals
  - on top of cabinets
  - on floor
  - in hoods
  - with food or drinks
  - in refrigerators used for food
  - where there are wide variations in temperature, humidity or sunlight

Chemical storage: Containers

- Don't use chemical containers for food
- Don't use food containers for chemicals
- Be sure all containers are properly closed
- Wipe off outside of container before returning to storage area
- Transport/carry all containers safety
  - Preferably use outer protective container

Improper chemical storage

Never use hallways for storage

Safety Hazard!!

Blocks exit path in emergencies!!!

Suggested shelf storage groups: Organics

- Acids, anhydrides
- Alcohols, amides, amines
- Aldehydes, esters, hydrocarbons
- Ethers, ketones, halogenated hydrocarbons
- Epoxies, isocyanates
- Azides, peroxides
- Nitriles, sulfides, sulfoxides
- Cresols, phenols

Suggested shelf storage groups: Inorganics

- Metals, hydrides
- Halides, halogens, phosphates, sulfates, sulfides
- Amides, azides, nitrates, nitrites
- Carbonates, hydroxides, oxides, silicates
- Chlorates, chlorites, perchlorates, peroxides
- Arsenates, cyanides, cyanates
- Borates, chromates, manganates
- Acids
- Arsenics, phosphorus, sulfur

Waste management: General guidelines

- Secure and lock waste storage area
- Post area
- Keep area well ventilated
- Provide fire extinguishers and alarms, spill kits
- Provide suitable PPE
- Provide eye wash, safety showers
- Do not work alone

Waste management: General guidelines

- Insure against leakage; dyke area if possible
- Label all chemicals, containers, vials
- Separate incompatible chemicals
- Keep gas cylinders separate
- Keep radioactive material separate
- Know how long waste can be stored
- Provide for timely pick up

Dangerous waste management

Waste management

- Recycle, reuse, redistill if possible
- Dispose by incineration, if possible
- Incineration is NOT the same as open burning

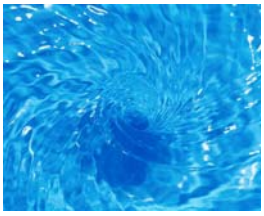
Waste management: Waste disposal service

- Is disposal service licensed?
- How will waste be transported?
- How will waste be packaged?
- Where will material be disposed?
- How will it be disposed?
- Maintain written records

Waste management: Down the drain?

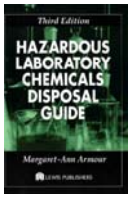
If legally allowed:

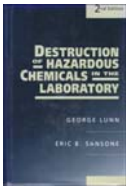
- Deactivate & neutralize some liquid wastes yourself
  - e.g., acids & bases
  - Don't corrode drain pipes
- Dilute with lots of water while pouring down the drain
- Be sure that you do not form more hazardous substances



Waste management: Treatment in Lab?

- **Destruction / neutralization of hazardous chemicals**
  - **May or may not be allowed by regulations**
  - **Must be done by trained chemist**
  - **Specific to each chemical**
- References:
  - "Procedures for the Laboratory-Scale Treatment of Surplus and Waste Chemicals, Section 7.D in Prudent Practices in the Laboratory: Handling and Disposal of Chemicals," National Academy Press, 1995, available online: http://www.nap.edu/catalog.php?record_id=4911
  - "Destruction of Hazardous Chemicals in the Laboratory, 2nd Edition", George Lunn and Eric. B. Sansone, Wiley Interscience, 1994, ISBN 978-0471573999
  - "Hazardous Laboratory Chemicals Disposal Guide, Third Edition", Margaret-Ann Armour, CRC Press, ISBN 978-1566705677
  - "Handbook of laboratory Waste Disposal", Martin J. Pitt and Eva Pitt, Ellis Horwood, 1985, ISBN 0-85312-634-8 (out of print)





Chemical management

- **Proper chemical management is an important part of laboratory safety and security**
- **Helps protect people, laboratories and the environment**
- **Can save money by avoiding duplicate chemical purchases**

Pesticide Management

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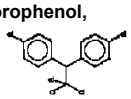
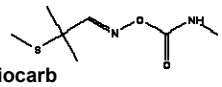
History of Pesticides

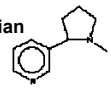
- **The first pesticides developed 4500 years ago: crop dusting with elemental sulfur.**
- **Modern pesticides**
  - **Main development/discovery period, 1870's to 1945.**
  - **DDT first synthesized in 1874, used as a pesticide in 1939, became the most widely used pesticide in the world.**
  - **Advances in organic chemistry and chemical engineering lead to mass production, especially after WWII.**
- **Uses**
  - **Health-Medical**
    - **Delousing, fumigation, precursors for pharmaceutical drugs.**
    - **Indoor spraying with DDT for malaria control recommended by WHO.**
    - **Used to prevent the spread of malaria, bubonic plague, sleeping sickness and typhus.**
  - **Agriculture**
    - **Pest control to prevent crop losses.**
    - **Financial advantage for farmers.**

Main pesticide categories

- **Organochlorines:**
  - **Chlordane, DDT, Dieldrin, 2,4,5-T, Lindane, Heptachlor, Pentachlorophenol, Endrin, Aldrin, Chlordecone, Endosulfan, Hexachlorobenzene, Methoxychlor, Mirex, Toxaphene, TDE.**
  - **Chemical warfare agents: sulfur mustard, HD.**
- **Organophosphates:**
  - **Esters of phosphoric acid, Parathion, Malathion, Methyl Parathion, Chlorpyrifos, Diazanon, Dichlorvos, Phosmet, Tetrachlorvinphos, Azinphos Methyl, Naled, Fenthion, Dimethoate, Acephate, phosalone and others.**
  - **Chemical warfare agents: sarin, tabun, soman and VX.**
- **Carbamates:**
  - **Carbaryl, Sevin, Aldicarb, Carbofuran, Furadan, Fenothiocarb**
- **Pyrethoids:**
  - **Synthetic chemical compound similar to natural pyrethins produced by the flowers of pyrethums (*Chrysanthemum cinerariaefolium* and *C. coccineum*).**
  - **Common in household insecticides and insect repellent. At concentrations used in such products, they are generally harmless to human beings, except sensitive individuals.**
- **Neo-nicotinoids:**
  - **Synthetic analogs of nicotine insecticides, exhibit much lower mammalian toxicity and greater field persistence.**
  - **Used in place of organophosphates and carbamates**





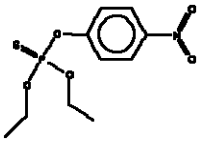


Red: banned by Stockholm Convention

Pesticides categorized by toxicity

Class		LD50 for the rat (mg/kg body weight)			
		Oral		Dermal	
		Solids	Liquids	Solids	Liquids
Ia	Extremely hazardous	≤ 5	≤ 20	≤ 10	≤ 40
Ib	Highly hazardous	5 - 50	20 - 200	10-100	40 – 400
II	Moderately hazardous	50 - 500	200 - 2000	100-1000	400 – 4000
III	Slightly hazardous	Over 500	Over 2000	Over 1000	Over 4000

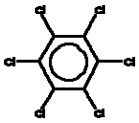
- Class Ia: Aldicarb, Hexachlorobenzene, Parathion
- Class Ib: Carbofuran, Dichlorvos, Nicotine
- Class II: Chlordane, Carbaryl, Chlorpyrifos, DDT, Naled
- Class III: Acephate, Fenothiocarb, Malathion



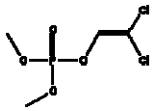
"The WHO Recommended Classification of Pesticides by Hazard and Guidelines to Classification, 2004", updated June 2006, http://www.who.int/ipcs/publications/pesticides_hazard_rev_3.pdf

Bad effects/properties of pesticides

- **Organochlorines**
  - Accumulates in human adipose tissue and human breast milk
  - Accumulates and persists in animal milk and dairy products
  - Interferes with estrogen and androgen receptors
  - Suppresses immune system
  - Targets sodium ion channels making powerful convulsants
  - Can induce neurobehavioral problems
  - Can cause cancer, possibly including breast cancer
  - Long term exposure linked to type 2 diabetes
  - Extremely long half life remaining ecologically active for years-to-decades once applied in the environment.



- **Organophosphates,**
  - Acts against the enzyme acetolcholinesterase or cholinesterase by irreversibly inactivating it.
  - Degrades much more quickly in the environment than organochlorines
  - Organophosphates are generally more toxic than organochlorines.
  - Most common source of poisoning world-wide.
  - Intentionally used for suicides in agricultural areas.
  - Closely related to chemical warfare 'nerve'agents (sarin, tabun, soman and VX).



Problems with pesticide use

- **Persistence**
  - Organochlorine pesticides resist degradation. Half-lives range from months to years to decades.
  - Organophosphates are less persistent in the environment, but tend to be more toxic to other species (including humans and warm-blooded animals).
  - Pesticides are found in surface and ground-waters, agricultural fields and farms, urban and suburban locations and undisturbed natural areas thought to be 'pristine'.
  - Pesticides used on crops have been found hundreds of miles downstream in drinking water that comes from rivers flowing through farmland

- **Non-discrimination**
  - Improper use or application leads to the elimination of all arthropod species and severe consequences for other wildlife.
  - Can contribute to the collapse of soil eco-systems by eliminating soil bacteria and funguses.
- **Resistance**
  - Long term or improper use of insecticides can produce resistance in target species.
  - In Sri Lanka, parts of India, Pakistan, Turkey and Central America, DDT resistance in mosquitoes has forced a shift to organophosphate and carbamate insecticides for malaria control.

International Organizations/Agreements concerned with pesticide problems

- United Nations Food and Agriculture Organization (FAO)
  - Founded in 1946.
  - Advises countries which import pesticides on how to manage them.
- Stockholm Convention on Persistent Organic Pollutants
  - Ratified by 134 nations; entered into force May 2001.
  - International agreement concerning Persistent Organic Pollutants (POPs), "chemical substances that persist in the environment, bio-accumulate through the food web, and pose a risk of causing adverse effects to human health and the environment".
  - Bans or severely restricts the production, use, trade and disposal of 12 POP's.
- Rotterdam Convention
  - Prior Informed Consent Procedure for Certain Hazardous Chemicals and Pesticides in International Trade (PIC Convention)
  - Ratified by 11 nations; entered into force February 2004.
  - Nations must know about imports of chemicals that are banned or severely restricted in the exporting country, or are severely hazardous pesticide formulations.
- Aarhus Protocol on Persistent Organic Pollutants
  - Amendment to the 1979 Geneva Convention on Long Range Trans-boundary Air Pollution.
  - Deals with Long Range Transport caused by the semi-volatile and persistent nature of these chemicals combined with global wind distribution.

Current Status

- Large stockpiles of obsolete pesticides are located in many developing countries.
- Many are beyond the manufacturers expiration date.
- Stocks are not inventoried or secured.
- Materials are routinely used by untrained applicators resulting in
  - over application
  - personal exposure
  - contamination of fields, farms, storage facilities and other people.

- http://www.fao.org/ag/AGP/AGPP/Pesticid/p.htm has useful information on Pesticide management.

Pesticide management issues: Global

- Large stockpiles of pesticides exist as a result of:
  - Changes in agricultural/environmental policies in developed nations
  - Ratification of several international treaties and conventions.
  - These pesticides considered 'obsolete' by the FAO.

- Many pesticides transferred to the developing world
  - Demand exists throughout the developing world
    - Especially DDT to combat malaria.
  - International manufacturers continue production
  - Large amounts of recently banned pesticide products from Europe and North America were freely given to any nation that asked for them.

Pesticide management issues: Local

- **Usage**
  - Pesticides all come with specific instructions for application.
  - Individuals applying these pesticides should be:
    - Well trained
    - Familiar with the inherent hazards posed by these chemicals.
    - Knowledgeable about regional soil conditions and pest organisms.
- **Application**
  - Bulk quantities can lack chemical property data and manufacturers instructions on utilization, application and precautions.
  - Some pesticide "systems" require the use of special emulsifiers for proper usage.
  - Excessive application due to lack of proper instructions occurs frequently.
  - Over-application is leading cause of human illness and water/soil contamination/degradation.

Pesticide management issues: Local

- **Storage**
  - Obsolete stocks of pesticides are found in long term storage, outdoors, exposed to the elements.
  - Intense sunlight, heat, humidity and precipitation lead to loss of potency.
  - Chemical weathering can produce toxic by-products.
  - Damaged containers lead to distribution by wind, storm run-off, theft and vandalism.
  - Obliterated labels lead to improper application and usage.
  - Stock piles should be stored out of direct sunlight or precipitation and under lock and key.

Pesticide management issues: Local

- **Disposal**
  - Proper disposal is time consuming and expensive.
  - Very few countries can properly dispose of these chemicals.
  - Until funding/infrastructure allow for proper local/regional disposal, provide physical protection for and limit access to these materials.
  - Improperly disposed of pesticides can:
    - Cause innocent people to become sick or to die from inadvertent exposure.
    - Can also cause livestock to become sick or to die.
    - Can make them easy to steal for criminal/ terrorism uses.

Obsolete Pesticide Recommendations

- Inventory
  - Many countries do not have central inventory sources
    - Makes it difficult to address the problem of disposal
    - Makes it easier for terrorists to steal pesticides
  - What do you have in your country?
    - Who knows the answers?
  - Is it usable or deteriorated?
  - Do you really need it? Will you really use it?
- Usable
  - Make safe/secure
  - Repackage/re-label if necessary
  - Store securely until use by trained personnel
- Not usable
  - Make safe/secure
  - Repackage/re-label if necessary
  - Store securely until proper disposal

Lab Safety Activity:

What's Wrong With These Pictures?

What's Wrong With This Picture?

What's Wrong With This Picture?

What's Wrong With This Picture?

What's Wrong With This Picture?

What's Wrong With This Picture?

What's Wrong With This Picture?

Break

REACH and the Global Harmonized System for the Labeling of Chemicals

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REACH

Registration, Evaluation, Authorisation of Chemicals

2007 EU regulation; replaces 40 existing acts to create a single system for all chemicals

- requires authorization to use, manufacture and import
- to track and manage chemical risks and provide safety information
- proposes to integrate REACH with GHS
- creates European Chemical Agency (ECHA, Helsinki, Finland

REACH

Life of the chemical from Cradle-to-the-Grave

Manufacturing

Importing

Marketing

Use

Waste stream

REACH

- Comprehensive legislation to ensure European authorities know and condone what chemicals are used as they enter the EU supply train
- Objective is to protect human health and the environment by recognizing and classifying hazardous chemicals so they are handled safely
- REACH & GHS are not equivalent or optional but separate legislation with parallel requirements

REACH

- The responsibility for proving whether a chemical is hazardous or non-hazardous is on the manufacturer and supplier not the government
- The responsibility also includes documentation, tests, classification, risk exposure, labeling, safety data sheets
- ECHA will store the information in the International Uniform Chemical information Database (IUCLID)

REACH

Four Steps

1. Registration
2. Evaluation
3. Authorization
4. Restriction

ECHA maintains database

REACH: Registration

Importers and manufacturers of substances in quantities over 1 ton/yr must register their substance with ECHA

Registration began June 2007

December 1, 2010

≥ 1000 tons per year

- **carcinogenic, mutagenic, or reproductive toxin ≥ 1 ton per year**
- **substances classified as dangerous for aquatic environment ≥ 100 tons per year**

June 1, 2013

- **manufactured or imported at 100-1000 tons per year**

June 1, 2018

- **manufactured or imported at 1-100 tons per year**

REACH: Evaluation

Authorities will review registration and request further information or testing to determine the impact of the substance on human health and the environment

Decides next steps:

-- action for authorization

-- align classification & label

-- other action

REACH: Authorization

Decisions on what substances require an authorization or restriction are carried out for substances that pose the most concern, such as carcinogens and mutagens

Three steps:

- **SVHC (Substances of Very High Concern)**
  - **carcinogenic, mutagenic and reprotoxic substances, persistent, bio-accumulative and toxic**
- **Prioritize**
- **Authorization provided**

REACH: Restriction

- Limit uses
  - Where no viable alternative exists, a research and development plan to derive a suitable alternative is developed
- Ban substance
  - where there is an unacceptable risk to human health and the environment.

REACH: Concern

A potential concern may be creating country specific safety data sheets and labels that are compatible with the GHS proposal

REACH: Resources

About REACH:
http://reach.jrc.it/about_reach_en.htm

REACH Help:
http://echa.europa.eu/reach/helpdesk_en.htm

About ECHA: http://ec.europa.eu/echa

http://ec.europa.eu/environment/chemicals/reach/reach_intro.htm

Globally Harmonized System for Classification and Labeling of Chemicals (GHS)

International UN standardization for classification, safety data sheet format, and labeling of chemicals using pictograms, signal words, and hazard warnings

US OSHA is reviewing GHS for adoption

GHS

- **United Nations proposed system to internationally standardize chemical communication**
- **Countries will adopt on their own timeframe**
- **2008 - UN goal for world-wide implementation**

GHS Implementation

Intergovernmental Forum on Chemical Safety (IFCS)- adopted GHS implementation goal of 2008. The US participates and agreed to work toward this goal

Japan, Korea, New Zealand – various stages of adopting & implemented GHS

European Union – 2010 deadline for GHS substance classification

Canada – Assessing how to adopt and implement GHS

United States – Assessing impact of GHS, plans to adopt GHS by 2009. DOT expects to have changes in place by 2009

GHS Benefits

- Uniform Communication
- Better Safety

- Improved International Trade
- Lower cost

GHS Changes

MSDS now named: “SDS” (Safety Data Sheet)

Labels will be standardized with:

- signal words
- hazard statements
- precautionary statements
- pictograms
- elimination of US, Canadian and EU labels

GHS Labeling

Information required on a GHS label:

- **Pictograms**
- **Signal words**
- **Hazard statements**
- **Precautionary statements and pictograms**
- **Product identifier**
- **Supplier information**

Changes to (M)SDS

GHS name: Safety Data Sheet (SDS)

- Format:
  - 16 sections required in specified order (as per ANSI MSDS format in US Regulations presentation)
- Reclassification:
  - (MSDS) Health & Physical Hazards
  - (SDS) Environmental Hazards
- Building Block Approach
  - each country can select portions of GHS to adopt
  - Not every country will require all categories or all hazards

Examples of GHS Pictograms

Differences between REACH and GHS

- REACH and GHS have different scopes but there are many links between the two regulations
- REACH aims to produces information on hazards, risks, and risk management
- GHS aims to harmonize classification and labeling of materials
- GHS is a UN recommendation which applies across countries, including the EU

Differences between REACH and GHS

- REACH intends to replace current EU classification criteria with GHS. REACH has provisions for safety data sheets based on GHS.
- GHS intends to apply classification and labeling beginning December 1, 2010, when the new GHS regulation will be available.
- Substances will be phased in the first 3.5 years. Mixtures will be given an additional 4.5 years for reclassification.

Globally Harmonized System

Resources

http://www.unece.org/trans/danger/publi/ghs/ghs_rev02/02files_e.html

http://www.unece.org/trans/danger/publi/ghs/presentation_e.html

http://www.osha.gov/SLTC/hazardcommunications/global.html

Chemical Dual-use Awareness and International Chemical Controls

Pauline Ho, PhD

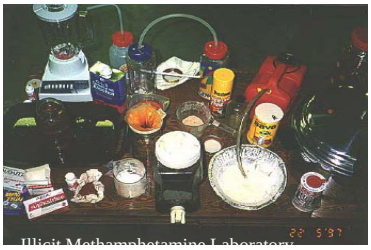
International Chemical Threat Reduction Department
Sandia National Laboratories

Chemical dual-use awareness

Dual use chemicals: Chemicals used in industry or everyday life that can also be used in bad ways.

Dual-use chemical example: Pseudoephedrine

- Pseudoephedrine is a common ingredient in cold medicines
- Precursor to crystal methamphetamine
- Recipes for conversion available on web



- Clandestine meth labs in US during 2002
  - Caused 194 fires, 117 explosions, and 22 deaths
  - Cost $23.8 million for cleanup
  - Dumped chemicals led to
    - deaths of livestock
    - contaminated streams
    - large areas of dead trees and vegetation

US DEA, http://www.deadiversion.usdoj.gov/pubs/brochures/pseudo/pseudo_trifold.htm, viewed Dec 2007

Dual-use chemical example: Cyanide

Therence Koh/AFP/Getty Images

- Widely used in mining and metal plating industries, but is also a well known poison.
- Product tampering*
  - Tylenol capsules
    - laced with KCN
    - 7 deaths, fall 1982, Chicago, Illinois, USA
    - Led to tamper-proof product packaging
- Popular with criminals and terrorists because it is relatively easy to obtain
- HCN is CW agent AC

* "Tylenol Crisis of 1982." *Wikipedia, The Free Encyclopedia*. 22 Nov 2007, 06:04 UTC. Wikimedia Foundation, Inc. 28 Nov 2007 <http://en.wikipedia.org/w/index.php?title=Tylenol_Crisis_of_1982&oldid=173056508>.

Dual-use chemical example: Pesticides

- Widely used in homes and agriculture, but also used to poison people.

FIGURE. Package of Chinese rodenticide implicated in the poisoning of a female infant aged 15 months — New York City, 2002

Photo/New York City Poison Control Center

- Dushuqiang (Strong Rat Poison)
  - Outlawed in China in the mid-1980s, but was still available
  - Nanjing, China, Sept. 2002
    - 38 people killed by poison in snack-shop food, >300 sick
    - Jealously by rival shop owner
  - Hunan, China, Sept. 2003
    - 241 people poisoned by cakes served by school cafeteria
    - Motive and perpetrator unknown
  - Tongchuan City, Shaanxi, China, April 2004
    - 74 people poisoned by scallion pancakes
    - Motive and perpetrator unknown
  - 5 other incidents reported between 1991 and 2004

Ann. Emerg. Med., Vol. 45, pg. 609, June 2005

Many lab/industrial chemicals have dual uses

- Dimethyl methyl phosphonate (DMMP)
  - Flame retardant for:
    - building materials, furnishings, transportation equipment, electrical industry, upholstery
  - Nerve agent precursor

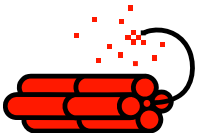
- Thiodiglycol
  - Dye carrier, ink solvent, lubricant, cosmetics, anti-arthritic drugs, plastics, stabilizers, antioxidants, photographic, copying, antistatic agent, epoxides, coatings, metal plating
  - Mustard gas precursor

- Arsenic Trichloride
  - Catalyst in CFC manufacture, semiconductor precursor, intermediate for pharmaceuticals, insecticides
  - Lewisite precursor

From: Chemical Weapons Convention: Implementation Assistance Programme Manual (on CD)

Dual-use Chemicals: Explosives

- Theft of conventional explosives
  - Chemical suppliers
  - Users such as mines or construction sites
- Diversion of industrial or laboratory chemicals
  - Chemical suppliers
  - Chemical factories
  - Academic teaching or research laboratories
  - Disposal sites



Theft / manufacture of explosives: Fertilizer Bomb

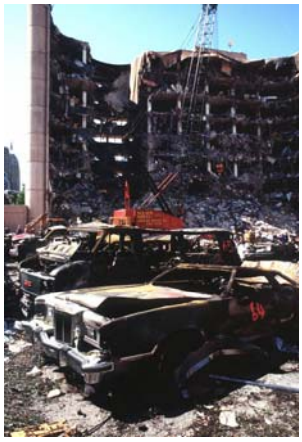


Photo: US DOD

- Ammonium nitrate fertilizer and fuel oil (diesel, kerosene)
- Used to bomb Alfred P. Murrah building in Oklahoma City, OK, USA
  - with nitromethane and commercial explosives
  - 168 dead, including children
  - April 1995
- Favored by IRA, FARC, ETA, etc.

Diversion of industrial / laboratory chemicals: Sodium azide

- **Widely available from older automobile airbags**
  - **1980s to 1990s**
- **Poisonous**
- **Reacts explosively with metals**
  - **Biological laboratory drains have exploded from discarded waste solutions containing NaN_3 as a preservative.**
- **Has been found in possession of terrorists**

Diversion of industrial / laboratory chemicals

- Malaysian police arrested 36-year-old Alias Osman on June 9, 2003 in a Kuala Lumpur suburb. They claim he was a member of the militant Islamic group Jemaah Islamiah (JI). Police say he led them to an oil-palm plantation where a cache of chemicals was buried, including an unspecified amount of sodium azide. Most of the chemicals seized, potassium chloride*, calcium chloride* and aluminum powder, were similar to those used in the Bali bomb blasts.**

* Should be chlorate, not chloride

** Different devices may have used different explosive mixtures. Analysis gave evidence for chlorate and TNT

Simon Elegant, "Poisonous Minds," Time (Asia) 161, June 30, 2003.
http://www.time.com/time/magazine/article/0,9171,501030630-460248,00.html, viewed Nov. 2007
D. Royds, S.W. Lewis, A.M. Taylor, Talanta 67 (2005) 262–268

Diversion of industrial / laboratory chemicals: Quote from the "Terrorists Handbook"

2.1 ACQUIRING CHEMICALS

The first section deals with getting chemicals legally. This section deals with "procuring" them. The best place to steal chemicals is a college. Many state schools have all of their chemicals out on the shelves in the labs, and more in their chemical stockrooms. Evening is the best time to enter lab buildings, as there are the least number of people in the buildings, and most of the labs will still be unlocked. One simply takes a bookbag, wears a dress shirt and jeans, and tries to resemble a college freshman. If anyone asks what such a person is doing, the thief can simply say that he is looking for the polymer chemistry lab, or some other chemistry-related department other than the one they are in.

9.0 CHECKLIST FOR RAIDS ON LABS

http://www.totse.com/en/bad_ideas/irresponsible_activities/168593.html, downloaded Nov. 2007

International chemical control groups

ORGANISATION FOR THE PROHIBITION OF CHEMICAL WEAPONS

Chemical weapons convention

The Australia Group

Export controls

UN Security Council Resolution 1540

Organization for the prohibition of chemical weapons (OPCW)

- International group headquartered in The Hague, Netherlands
  - https://www.opcw.org/index.html
- Chemical weapons convention (CWC)
  - International treaty which bans the development, production, stockpiling, transfer and use of chemical weapons
- Promotes international cooperation in peaceful uses of chemistry
- Protecting each other

Chemical Weapons Convention (CWC)

- International treaty which bans the development, production, stockpiling, transfer and use of chemical weapons
  - Entered into force in April 1997 with 87 State Parties participating
  - Today: 183 nations have joined, 5 others have signed, only 7 have not taken any action.
    - Each nation enacts appropriate laws
    - Each nation agrees to assist other Member States

CWC: Destroy existing stockpiles and facilities

- Twelve States parties have declared CW production facilities.
  - Bosnia and Herzegovina
  - China
  - France
  - India
  - Islamic Republic of Iran
  - Japan
  - Libyan Arab Jamahiriya
  - Russian Federation
  - Serbia
  - United Kingdom of Great Britain and Northern Ireland
  - United States of America
  - another State Party
- As of August 2007, 42 of 65 declared CW production facilities have been certified as destroyed, 19 converted to peaceful purposes.
- As of August 2007, 23,912 metric tonnes of CW agent has been destroyed out of 71,330 metric tonnes declared.
- On 11 July 2007, the OPCW confirmed the destruction of the entire chemical weapons stockpile in Albania.
- Includes old and abandoned CW munitions

CWC: Prevent spread or production of new chemical weapons

- States declare and agree to inspections of many other chemical facilities, depending on chemical type and amount produced
- Over 3,000 inspections have taken place at 200 chemical weapon-related and over 850 industrial sites on the territory of 79 States Parties since April 1997
- Worldwide, over 5,000 industrial facilities are liable to inspection

CWC: Chemicals on schedules subject to verification measures

- Schedule 1:
  - Known CW agents
  - Highly toxic, closely related chemicals, or CWA precursors
  - Has little or no peaceful application
- Schedule 2:
  - Toxic enough to be used as a CWA
  - Precursor to or important for making a Schedule 1 chemical
  - Not made in large commercial quantities for peaceful purposes
- Schedule 3:
  - Has been used as a CWA
  - Precursor to, or important for making a Schedule 1 or 2 chemical
  - Is made in large commercial quantities for peaceful purposes
- Unscheduled Discrete Organic Chemicals (UDOC)
- Lists of scheduled chemicals follow: also in documents on CD

CWC: Reporting requirements

- Use/transfer of these chemicals is allowed for research, medical, or pharmaceutical purposes.
- Reporting requirements depend on facility type, chemical types and amounts.
  - "Other Facility" type, as defined in CWC documents, most relevant here
  - Amounts of chemicals that would require that your National Authority approve the work and report your institution annually to the OPCW
    - Schedule 1: 100 g aggregate
    - Schedule 2: 1 kg for 2A*, 100 kg for other 2A, 1 Tonne of 2B
    - Schedule 3: 30 Tonnes
    - UDOC: 30 or 200 Tonnes (lower number if contains P, S, or F)

Caution:
Your country might require reporting of lower amounts!

Schedule 1 Chemicals

A. Toxic chemicals

- (1) O-Alkyl (<C10, incl. cycloalkyl) alkyl (Me, Et, n-Pr or i-Pr)-phosphonofluoridates, e.g.
  - Sarin: O-Isopropyl methylphosphonofluoridate
  - Soman: O-Pinacolyl ethylphosphonofluoridate
- (2) O-Alkyl (<C10, incl. cycloalkyl) N,N-dialkyl (Me, Et, n-Pr or i-Pr) phosphoramidocyanidates, e.g. Tabun: O-Ethyl N,N-dimethyl phosphoramidocyanidate
- (3) O-Alkyl (H or <C10, incl. cycloalkyl) S-2-dialkyl (Me, Et, n-Pr or i-Pr)-aminoethyl alkyl (Me, Et, n-Pr or i-Pr) phosphonothiolates and corresponding alkylated or protonated salts, e.g. VX: O-Ethyl S-2-diisopropylaminoethyl methyl phosphonothiolate
- (4) Sulfur mustards:
  - 2-Chloroethylchloromethylsulfide
  - Mustard gas: Bis(2-chloroethyl)sulfide
  - Bis(2-chloroethylthio)methane
  - Sesquimustard: 1,2-Bis(2-chloroethylthio)ethane
  - 1,3-Bis(2-chloroethylthio)-n-propane
  - 1,4-Bis(2-chloroethylthio)-n-butane
  - 1,5-Bis(2-chloroethylthio)-n-pentane
  - Bis(2-chloroethylthiomethyl)ether
  - O-Mustard: Bis(2-chloroethylthioethyl)ether
- (5) Lewisites:
  - Lewisite 1: 2-Chlorovinyldichloroarsine
  - Lewisite 2: Bis(2-chlorovinyl)chloroarsine
  - Lewisite 3: Tris(2-chlorovinyl)arsine
- (6) Nitrogen mustards:
  - HN1: Bis(2-chloroethyl)ethylamine
  - HN2: Bis(2-chloroethyl)methylamine
  - HN3: Tris(2-chloroethyl)amine
- (7) Saxitoxin
- (8) Ricin

B. Precursors

- (9) Alkyl (Me, Et, n-Pr or i-Pr) phosphonyldifluorides, e.g. DF: Methylphosphonyldifluoride
- (10) O-Alkyl (H or <C10, incl. cycloalkyl) O-2-dialkyl (Me, Et, n-Pr or i-Pr)-aminoethyl alkyl (Me, Et, n-Pr or i-Pr) phosphonites and corresponding alkylated or protonated salts e.g. QL: O-Ethyl O-2-diisopropylaminoethyl methylphosphonite
- (11) Chlorosarin: O-Isopropyl methylphosphonochloridate
- (12) Chlorosoman: O-Pinacolyl methylphosphonochloridate

Schedule 2 Chemicals

A. Toxic chemicals

- (1) Amiton: O,O-Diethyl S-[2-(diethylamino)ethyl] phosphorothiolate and corresponding alkylated or protonated salts
- (2) PFIB: 1,1,3,3,3-Pentafluoro-2-(trifluoromethyl)-1-propene
- (3) BZ: 3-Quinuclidinyl benzilate

B. Precursors

- (4) Chemicals, except for those listed in Schedule 1, containing a phosphorus atom to which is bonded one methyl, ethyl or propyl (normal or iso) group but not further carbon atoms, e.g.
  - ethylphosphonyl dichloride
  - dimethyl methylphosphonate
  - Exemption: Fonofos: O-Ethyl S-phenyl ethylphosphonothiolothionate
- (5) N,N-Dialkyl (Me, Et, n-Pr or i-Pr) phosphoramidic dihalides
- (6) Dialkyl (Me, Et, n-Pr or i-Pr) N,N-dialkyl (Me, Et, n-Pr or i-Pr)-phosphoramidates
- (7) Arsenic trichloride
- (8) 2,2-Diphenyl-2-hydroxyacetic acid
- (9) Quinuclidin-3-ol
- (10) N,N-Dialkyl (Me, Et, n-Pr or i-Pr) aminoethyl-2-chlorides and corresponding protonated salts
- (11) N,N-Dialkyl (Me, Et, n-Pr or i-Pr) aminoethane-2-ols and corresponding protonated salts
  - Exemptions: N,N-Dimethylaminoethanol and corresponding protonated salts
  - N,N-Diethylaminoethanol and corresponding protonated salts
- (12) N,N-Dialkyl (Me, Et, n-Pr or i-Pr) aminoethane-2-thiols and corresponding protonated salts
- (13) Thiodiglycol: Bis(2-hydroxyethyl)sulfide
- (14) Pinacolyl alcohol: 3,3-Dimethylbutan-2-ol

Schedule 3 Chemicals

A. Toxic chemicals

- (1) Phosgene: Carbonyl dichloride
- (2) Cyanogen chloride
- (3) Hydrogen cyanide
- (4) Chloropicrin: Trichloronitromethane

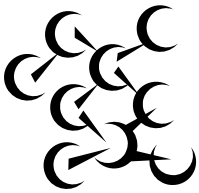
B. Precursors

- (5) Phosphorus oxychloride
- (6) Phosphorus trichloride
- (7) Phosphorus pentachloride
- (8) Trimethyl phosphite
- (9) Triethyl phosphite
- (10) Dimethyl phosphite
- (11) Diethyl phosphite
- (12) Sulfur monochloride
- (13) Sulfur dichloride
- (14) Thionyl chloride
- (15) Ethyldiethanolamine
- (16) Methyldiethanolamine
- (17) Triethanolamine

Unscheduled discrete organic chemicals (UDOC)

- Also subject to CWC reporting, but only for large amounts.
- "Discrete Organic Chemical" means any chemical belonging to the class of chemical compounds consisting of all compounds of carbon except for its oxides, sulfides and metal carbonates, identifiable by chemical name, by structural formula, if known, and by Chemical Abstracts Service registry number, if assigned.

From CWC text – on CD

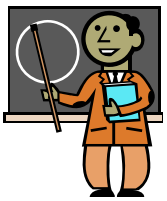


OPCW: Promotes international cooperation in peaceful uses of chemistry

- Associates program
- Analytical skills development course
- Conference support program
- Research projects program
- Internship Support Program
- Laboratory Assistance Program
- Equipment Exchange Program

OPCW: Protecting each other

- Each member state can request assistance from other member states in the event of a threat or attack, including chemical terrorism
- This can take the form of expertise, training, materials, and/or equipment



Australia Group

- An informal arrangement to minimize the risk of assisting chemical and biological weapon (CBW) proliferation.
  - Harmonising participating countries' national export licensing measures
  - Started in 1985 when Iraq CW program was found to have diverted chemicals and equipment from legitimate trade
- 40 nations plus European Commission participate

Australia Group: Export Controls

- Controls exports of:
  - 63+ Chemical weapon agent precursor chemicals
  - Dual-use chemical manufacturing facilities and equipment and related technology
  - Dual-use biological equipment and related technology
  - Biological agents
  - Plant pathogens
  - Animal pathogens

- Includes no-undercut policy
  - Countries won't approve an export that another member country denied

UN Security Council Resolution 1540

- Unanimously passed on 28 April 2004
- Member States:
  - must refrain from supporting non-State actors in developing, acquiring, manufacturing, possessing, transporting, transferring or using nuclear, chemical or biological weapons and their delivery systems.
  - must establish domestic controls to prevent the proliferation of nuclear, chemical and biological weapons, and their means of delivery, including by establishing appropriate controls over related materials.
- Enhanced international cooperation on such efforts is encouraged, in accord with and promoting universal adherence to existing international non-proliferation treaties.

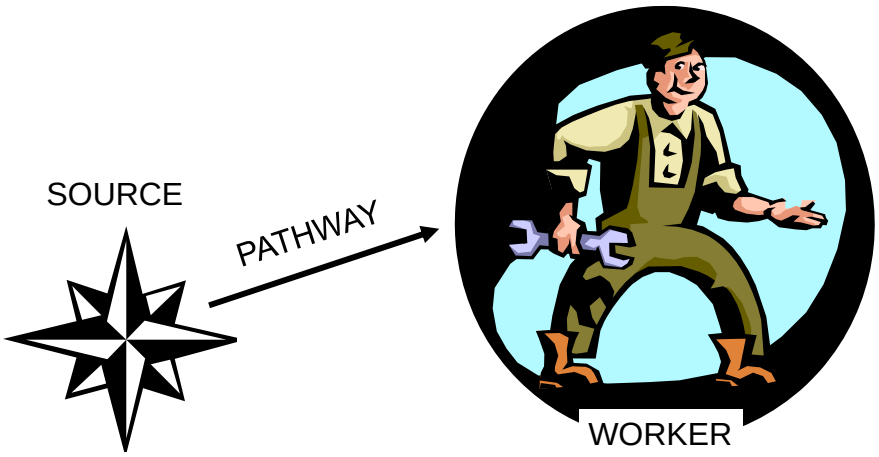
Controlling Hazards:

Personal Protective Equipment (PPE) and Safety Equipment Performance Specifications

Douglas B. Walters, Ph.D., CSP, CCHO

Environmental & Chemical Safety Educational Institute

Worker Protection



Personal Protective Equipment (PPE)

- **Always 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:

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

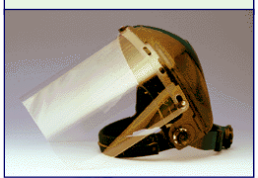
Eye & Face Protection

- 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



Hazard Assessment

Hazard Type	Hazard Source	Common Associated 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**

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

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*

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

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 in selection process

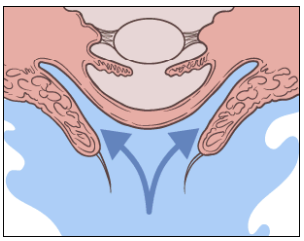
Eyewash and Showers

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

Eyewash and Showers

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

Eye & Face Protection



- Eye wash stations
  - minimum 0.4 to 3.5 gal/min
    - flush for 15 minutes
  - provide flow for both eyes
    - hold eyes open
    - tepid, pH match eye (preferred)
  - easily accessible locations
    - 33 to 45 inches from floor
    - 6 inches from wall
  - test weekly
    - portable: clean/refill (6 mo – 2 yrs)
  - various types

ANSI Z358.1
NC DOL Guide:
www.dol.state.nc.us/osha/etta/indguide/ig28.pdf

Safety Showers

- within 55 feet or 10 seconds
  - Normal walking = 3.8 mph
- test monthly
- pull within reach (highly visible)
  - 82 to 96 inches high
  - deliver 20 inch column @ 60” above floor
- 20 - 30 gal/min (tepid: 60 to 100 °F)
- drains
- blankets/modesty curtains
- avoid or protect electrical outlets
- ANSI Z358.1-2004

Blocked Eyewash & Safety Shower

Dirty Eyewash Station

Poorly Maintained Eye Wash Station

Hand Protection

- Glove considerations
  - type
    - 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)**

Chemical Protection Ratings

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

http://www.hazmat.msu.edu:591/glove_guide/

Gloves

- It's important to have the *right glove* for the job and know *how long* it will last

- **Glove Charts:**
  - Consider several glove manufacturer's 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 BARRIER			NITRILE SOL-VEX			UNSUPPORTED NEOPRENE 29-865			SUPPORTED POLYVINYL ALCOHOL PVA			POLYVINYL CHLORIDE (Vinyl) SNORKEL			NATURAL RUBBER CANNERS AND HANDLERS*			NEOPRENE/ NATURAL RUBBER BLEND CHEMI-PRO*		
	Degradation Rating	Permeation: Breakthrough	Permeation: Rate	Degradation Rating	Permeation: Breakthrough	Permeation: Rate	Degradation Rating	Permeation: Breakthrough	Permeation: Rate	Degradation Rating	Permeation: Breakthrough	Permeation: Rate	Degradation Rating	Permeation: Breakthrough	Permeation: Rate	Degradation Rating	Permeation: Breakthrough	Permeation: Rate	Degradation Rating	Permeation: Breakthrough	Permeation: Rate
1. Acetaldehyde	■	380	E	P	—	—	E	10	F	NR	—	—	NR	—	—	E	7	F	E	10	F
2. Acetic Acid	■	150	—	G	270	—	E	60	—	NR	—	—	F	180	—	E	110	—	E	260	—
3. Acetone	▲	>480	E	NR	—	—	E	10	F	P	—	—	NR	—	—	E	10	F	G	10	G
4. Acetonitrile	▲	>480	E	F	30	F	E	20	G	■	150	G	NR	—	—	E	4	VG	E	10	VG
5. Acrylic Acid	—	—	—	G	120	—	E	390	—	NR	—	—	NR	—	—	E	80	—	E	65	—
6. Acrylonitrile	E	>480	E	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
7. Allyl Alcohol	▲	>480	E	F	140	F	E	140	VG	P	—	—	P	60	G	E	>10	VG	E	20	VG
8. Ammonia Gas	■	19	E	▲	>480	—	▲	>480	—	—	—	—	■	6	VG	—	—	—	■	27	VG
9. Ammonium Fluoride, 40%	—	—	—	E	>360	—	E	>480	—	NR	—	—	E	>360	—	E	>360	—	E	>360	—
10. Ammonium Hydroxide	E	30	—	E	>360	—	E	250	—	NR	—	—	E	240	—	E	90	—	E	240	—
11. Amyl Acetate	▲	>480	E	E	60	G	NR	—	—	G	>360	E	P	—	—	NR	—	—	P	—	—
12. Amyl Alcohol	—	—	—	E	30	E	E	290	VG	G	180	G	G	12	E	E	25	VG	E	45	VG
13. Aniline	▲	>480	E	NR	—	—	E	100	P	F	>360	E	F	180	VG	E	25	VG	E	50	G
14. Aqua Regia	—	—	—	F	>360	—	G	>480	—	NR	—	—	G	120	—	NR	—	—	G	180	—
15. Benzaldehyde	▲	>480	E	NR	—	—	NR	—	—	G	>360	E	NR	—	—	G	10	VG	G	25	F
16. Benzene, Benzol	▲	>480	E	P	—	—	NR	—	—	E	>360	E	NR	—	—	NR	—	—	NR	—	—
17. Benzotrichloride	—	—	—	E	>480	E	NR	—	—	—	—	—	—	—	—	NR	—	—	NR	—	—
18. Benzotrifluoride	—	—	—	E	170	G	F	—	—	E	—	—	G	<10	F	P	50	G	—	—	—
19. Bromine Water	—	—	—	E	>480	E	E	>480	E	—	—	—	—	—	—	—	—	—	—	—	—
20. 1-Bromopropane	▲	>480	E	■	23	F	■	<10	P	▲	>480	E	■	<10	F	■	<10	P	■	<10	P

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)

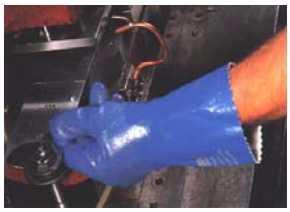
Types of Gloves

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

PVC

- protects against acids, caustics, oils, fats, petroleum hydrocarbons
- resists alcohols, glycols
- useful for:
  - 10% citric acid; cyclohexane, ethylene glycol, formaldehyde, formic acid, glycerine, 10% HCl
- ***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

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 (cause glove deterioration)
  - recognize the symptoms of latex allergy
  - always wash hands after removing gloves

www.cdc.gov/niosh/latexfs.html
www.osha-slc.gov/SLTC/latexallergy/index.html
http://www.nursingworld.org/osh/latex.htm

Proper steps for removing gloves

1

2

3

4

5

6

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)**

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

Types of Respirators

- Air Purifying (APR)
  - half Face
  - full Face
  - PAPR
- Air Supply
  - air line
  - SCBA






Air Purifying Respirators

- *Must have at least 19.5% oxygen*
  - *Never* **use in O_2 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**

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***

Cartridge Selection

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

End of Service Life Indicators

- **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

Assigned Protection Factors

- 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

Maximum Use Concentration (MUC)
= APF x Exposure Limit (TLV or PEL)

New Assigned Protection Factors

Type of Respirator	Quarter Mask	Half Face Mask	Full Facepiece	Helmet/ Hood	Loose-Fitting Facepiece
Air-Purifying	5	10	50	-	-
PAPR	-	50	1,000	25/1,000	25
Supplied-Air or Airline – Demand – Continuous flow – Pressure Demand	 - - -	 10 50 50	 50 1,000 1,000	 - 25/1000 -	 - 25 -
SCBA – Demand – Pressure Demand	 - -	 10 -	 50 10,000	 50 10,000	 - -

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) = APF x PEL
Quarter Mask: MUC = 1 ppm x 5 = 5 ppm
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

Dust Masks *vs.* Hospital Masks

High Efficiency Particulate Air Filter (HEPA) Respirator

Fit Testing

- **Qualitative**
  - **irritant smoke (stannic chloride)**
  - **isoamyl acetate (banana oil)**
  - **saccharin**
  - **bitrex**
  - *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/m^3 or less
  - CO ≤ 10 ppm or less
  - CO_2 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 facepiece:
  - dispose after use
- Half-mask:
  - write expiration date (current date + 30) 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 by 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

Body protection for emergency response

- Full suits
  - Class A
  - Class B
  - Class C
  - Class D

Level A Protective Suits

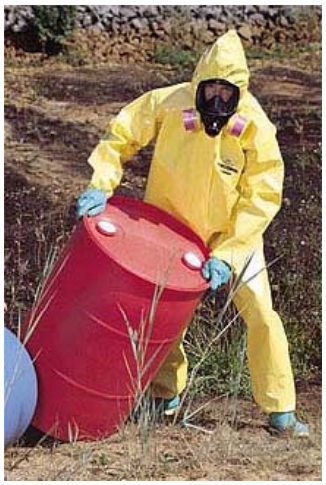
- potential exposure to unknown
  - greatest level of skin, respiratory, and eye protection
  - positive-pressure, full face-piece self contained breathing apparatus (SCBA) or positive pressure supplied air respirator with escape SCBA
  - totally encapsulated (air-tight) chemical and vapor protective suit
  - inner and outer chemical-resistant gloves, and boots

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**

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 between 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

Any Questions?