Chemical Safety and Security Workshop

Pekanbaru, Riau, Indonesia

July 2011

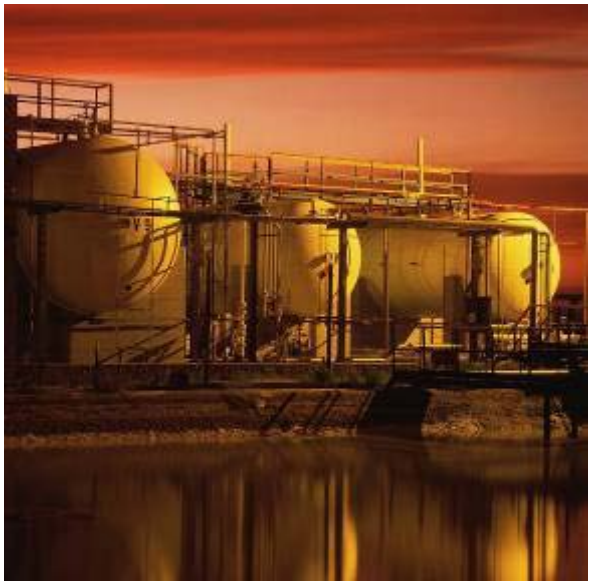
SAND No. 2009-8395P
Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Sandia National Laboratories

Chemical Safety and Security Overview

Why worry about chemical safety?

- **Chemicals used everyday in labs and factories can be hazardous.**



Studies indicate lab chemists *may* have:

- **Shorter life spans, more disease**

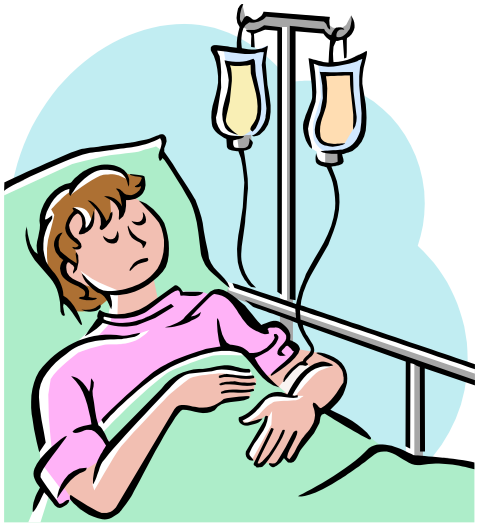
  Hoar, S. K. et al, *J. Occup. Med,.* 23, 485 (1981)

- **Higher cancer incidence**

  Dement J.M. & Cromer J.R., *Appl. Ocup. Environ. Hyg*., 7,120 (1992)

- **Higher suicide rate (females)**

  Walrath J. et al, *Amer. J. Pub. Health*, 35, 883 (1985)



Possible chemical health problems

Chemicals

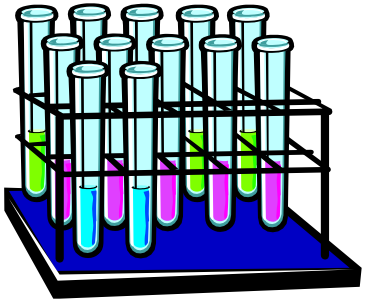
- Vinyl chloride
- Asbestos
- Carbon tetrachloride
- Mercury
- Lead
- Thalidomide
- Methanol
- CO, CS_2

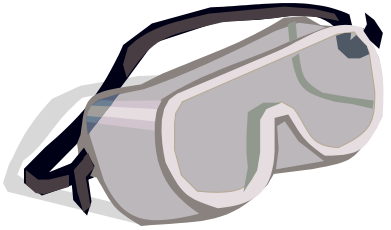
Diseases

- Liver cancer
- Mesothelioma
- Hepatotoxin (jaundice)
- Neurotoxin, CNS, narcosis
- Reprotoxin, birth defects
- Reprotoxin, developmental defects
- Blindness, death
- Hematopoietic, hemoglobin, cynanosis

But disease depends on many factors…

- Genetics
- Specific chemical
- Protection controls used
- Dose
- Concentration
- Duration
- Life style
- Environment





University of California Santa Cruz: Fire

- **January 11, 2002: about 5:30 am, 4th floor of Sinsheimer Lab building, Dept. of Molecular, Cell and Developmental Biology.**
  - Firefighters responded to alert from heat-detection system in building.
  - Controlled by noon.
  - Up-to-date inventory of hazardous materials allowed firefighters to enter building and contain fire.
  - Building did not have automatic sprinkler system.

http://ehs.ucsc.edu/emergency/pubs/sinshfire2.htm

University of California Santa Cruz: Fire, cont'd.

- **Professors and students lost equipment, notes, materials, samples.**
- **Other labs in building closed for weeks to months.**
  - Water and smoke damage
- **Burned labs took 2 years to reopen.**
- **Cause never determined.**

Environmental hazards
California State Univ. Northridge: Earthquake

- Magnitude 6.7
- January 17, 1994 – 4:31 am
- 57 deaths, 11000 injuries

- Epicenter a few km from California State University Northridge campus

- Several fires in science buildings allowed to burn because firemen worried about chemical hazards

- Professors and students lost equipment, notes, materials, samples

Images courtesy: P.W. Weigand, California State University Northridge Geology Department, Image source: Earth Science World Image Bank http://www.earthscienceworld.org/images

University lab chemical accidents

Incident – Chemical

- **Fire and one death –** t-butyl lithium + pentane
- **Dartmouth, wrong gloves –** methyl mercury
- **Wroclaw Poland, explosion –** dry perchlorates
- **Australia, skin absorption –** hydrofluoric acid
- **Okazaki Japan, explosion –** peroxide by-products in synthesis
- **OSU, US cylinder explosion –** liquid nitrogen cylinder
- **Material science engineering lab explosion –** nitric acid + ethanol explosion

Bhopal: Pesticide plant chemical release

- **One of the greatest chemical disasters in history, December 1984**
- **Union Carbide plant making Sevin released ~40 tonnes of methyl isocyanate in the middle of the night**
- **Low local demand for pesticides meant the plant was only partially running**
- **Some hardware was broken or turned off, including safety equipment**
  - Safety measures and equipment far below US standards
- **Plant in heavily populated area**

* "The Bhopal disaster and its aftermath: a review", Edward Broughton, *Environmental Health: A Global Access Science Source* 2005, **4**:6, http://www.ehjournal.net/content/4/1/6, accessed 12/07

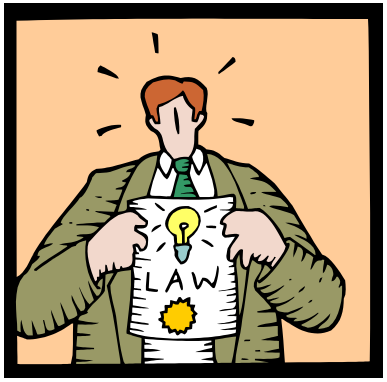
Safety Video: Reactive Hazards

Major industrial chemical disasters

Accident/location	Chemical product & exposure
~1912 Toyama Japan	itai-itai disease/cadmium
1921 Oppau Germany	ammonium nitrate
1930 Gauley Bridge WV USA	silica
1968 Yusho Japan	rice oil/PCB,PDDF
1974 Flixborough UK	cyclohexane
1976 Seveso Italy	herbicide production/TCDD
1984 Bhopal India	methyl isocyanate
1986 Chernobyl Ukraine	ionizing radiation
2005 Texas City USA	hydrocarbon production
2005 Jilin China	benzene/aniline

Chemical accidents are now under stricter control and scrutiny

- **Better individual country regulations**
- **Better international regulations**
  - IATA
  - GHS
  - REACH
- **Environmental problems after natural disasters**
  - Earthquakes, cyclones, hurricanes, floods
- **Increased public awareness**
- **Increased media coverage**
- **Less public tolerance**



Why worry about chemical safety?

- Health of the workers
- Safety of the workers
- Safety of the community
- Safety of the environment

…It's the right thing to do!

Why worry about chemical security?

- Long history of people deliberately using chemicals to harm others.
- Information on how to acquire and deliver them is easy to get:

Aum Shinrikyo: Matsumoto and Tokyo, Japan

- **Sarin attack on Judges in Matsumoto, June 1994**
  - Sarin sprayed from truck at night
  - 7 deaths, 144 injuries

- **Sarin attack on Tokyo subway, March 1995**
  - 11 bags with 600 g each on 3 main subway lines
  - 12 deaths, 3938 injuries

- **Hydrogen cyanide attacks on Tokyo subway, May 1995**
  - Bags of NaCN and sulfuric acid
  - No deaths, 4 injuries

Photo of wanted poster from Wikipedia commons

Aum Shinrikyo: Tokyo, Japan

Aum Shinrikyo: Matsumoto and Tokyo, Japan, cont'd.

- Recruited young scientists from top Japanese universities.
- Produced sarin, tabun, soman, VX.
- Purchased tons of chemicals through cult-owned companies.
- Motives: proof of religious prophecy, kill opponents, interfere with legal proceedings and police investigations.

Iraq

- **Many incidents in which chlorine gas cylinders are blown up with explosives**
  - Chlorine probably stolen/diverted from water purification plants or oil industry
  - Many civilians and non-combatants injured
- **Chlorine first used in WWI as a chemical weapon**

On March 23, 2007, police in Ramadi's Jazeera district seized a truck filled with "five 1000-gallon barrels filled with chlorine and more than two tons of explosives"

From http://www.longwarjournal.org/archives/2007/03/al_qaedas_chlorine_w.php downloaded Jan 2008.

Why worry about chemical security?

- **Health and safety of people and environment**
- **Community relationships**
- **Reduce chance of accidental chemical release**
- **Avoid loss and damage to labs and equipment**
- **Prevent criminals and terrorists from getting dangerous chemicals**
  - Wide variety of chemicals have been used
  - Wide variety of motivations for actions
- **A deliberate attack on a chemical facility could release a large amount of hazardous chemicals**
  - Injure or kill people in nearby areas
  - Eliminate jobs and economic assets

Safety and Security Issues are similar

Variables

- **Many different chemicals with:**
  - different properties
  - different hazard
  - different applications
- **Many different ways to misuse chemicals**
  - chemical weapons
  - poisons

Protect

- **Workers**
- **Facility**
- **Community**
- **Environment**

Government regulations: Chemical security

- **Differ from country to country**
- **Legislation needed to fulfill requirements under the Chemical Weapons Convention**
  - Each country passes appropriate laws
  - Each country must declare and track certain chemicals
- **UN Resolution 1540**
- **Other export control legislation**

Important Questions:

How does your country regulate and control chemical safety and security?

…Is it effective?

…Could it be improved?

…How?

Fundamentals of

Chemical Laboratory Safety

References

“Safety in Academic Laboratories, Vol.1 & 2,” American Chemical Society, Washington DC, 2003, also available online: http://membership.acs.org/c/ccs/publications.htm

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

Definitions

Chemical Laboratory Safety

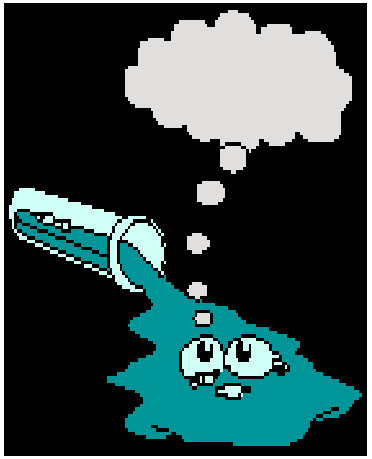
– ***The control of exposure to potentially hazardous substances to attain an acceptably low risk of exposure***

Chemical Laboratory Safety

Hazard – *the potential to harm*

Risk – *the probability that harm will result*

Chemical Laboratory Hazards



- **Chemical hazards**
  - dusts, fumes, mists, vapors, gases
- **Physical hazards**
  - fire, electrical, radiation, pressure vibration, temperatures, noise
- **Ergonomic hazards**
  - repetitive motion (pipetting), lifting, work areas (computers, instruments)
- **Biological hazards**
  - pathogens, blood or body fluids

Chemical Laboratory Safety

based on the principle of

Industrial Hygiene

– *The **anticipation, recognition, evaluation** and **control** of health hazards in the work environment to protect workers health and well-being and to safeguard the community and the environment*

Chemical Laboratory Safety

Industrial Hygiene Principles

Anticipation

Recognition

Evaluation

Control

Chemical hazards

Physical hazards

Ergonomic hazards

Biological hazards

Anticipation

Safety First !

To consider safety in the beginning is:

Easier,

Cheaper,

Safer,

… and it saves you time !

Anticipation

Advance Experiment Planning:

Outline proposed experiment

Acquire safety information (M)SDS, REACH

Consult with CSSO?

Anticipation

Risk Analysis

- Which chemicals?
- How much?
- Special equipment needed?
- Who does the work?
- Staff properly trained?
- Can the experiment go wrong?
- Do you have an emergency plan?

Recognition

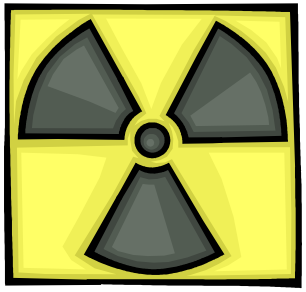
Types of lab hazards:

chemical toxicity

fire / explosion

physical hazards

biohazards



radiation

special substances

Recognition & Evaluation

What are the anticipated risks?

- Are the equipment & facilities adequate?
- Are staff properly and sufficiently trained?
- Risks if experiment goes wrong?
- Is there a plan for this?

Control

How are the risks controlled?

- **Engineering controls:**
  - enclosure / isolation
  - ventilation / hoods

- **Emergency Plan**

- **Personal Protective Equipment (PPE)**

Evaluation & Control

– **Administrative practices**

organizational policies

– **Operational practices**

work practices

– **Engineering controls**

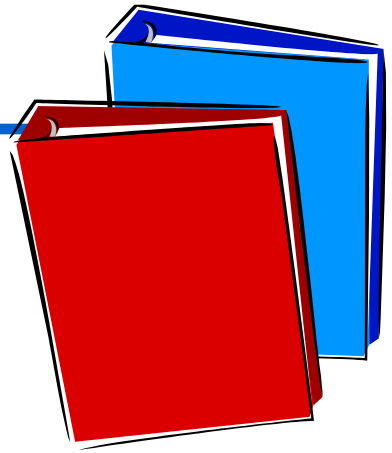
ventilation, barriers

Administrative Practices

organizational *safety policies*

that apply to everyone

Lab Safety Policies



❖ Have a Safety Manual

- Never work alone, especially after hours.
- Specify when eye protection & PPE is required.
- Specify operations that require hood use.
- Specify required training.
- No mouth pipetting.
- No long hair or dangling attire.

Lab Safety Policies

- No eating, drinking, smoking in laboratories
- Label all chemical containers
- Label refrigerators, No Food
- Label explosion safe refrigerators
- Require periodic fire drills

Lab Safety Policies

- **Schedule routine, periodic maintenance and inspection of hoods.**

- **Schedule routine, periodic maintenance of safety showers and eye wash stations.**

- **Post restricted areas with proper signs:**
  - radiation, biosafety, carcinogen, high voltage, lasers, authorized personnel only, etc.

Operational Practices

Safe Laboratory Procedures:

- Packages opened only in labs, not receiving
- Receiving staff trained to look for signs of breakage and/or leaking shipments
- Receiving area has spill kits
- Mailroom/receiving alert for suspicious shipments

Safe Laboratory Procedures

- Schedule routine maintenance, calibration and inspection of all hoods and safety equipment.

- Schedule and participate in routine fire drills.
- Train personnel in emergency response.

- Wear PPE <u>properly</u>, don't just have it.

Safe Laboratory Procedures

Use hoods properly:

- Work 6” (15 cm) in from sash
- In center of hood
- Work with hood sash at ~18” (45 cm) high
- Close sash when not in use
- Don’t use for storage

Safe Laboratory Procedures

Safely transport chemicals:

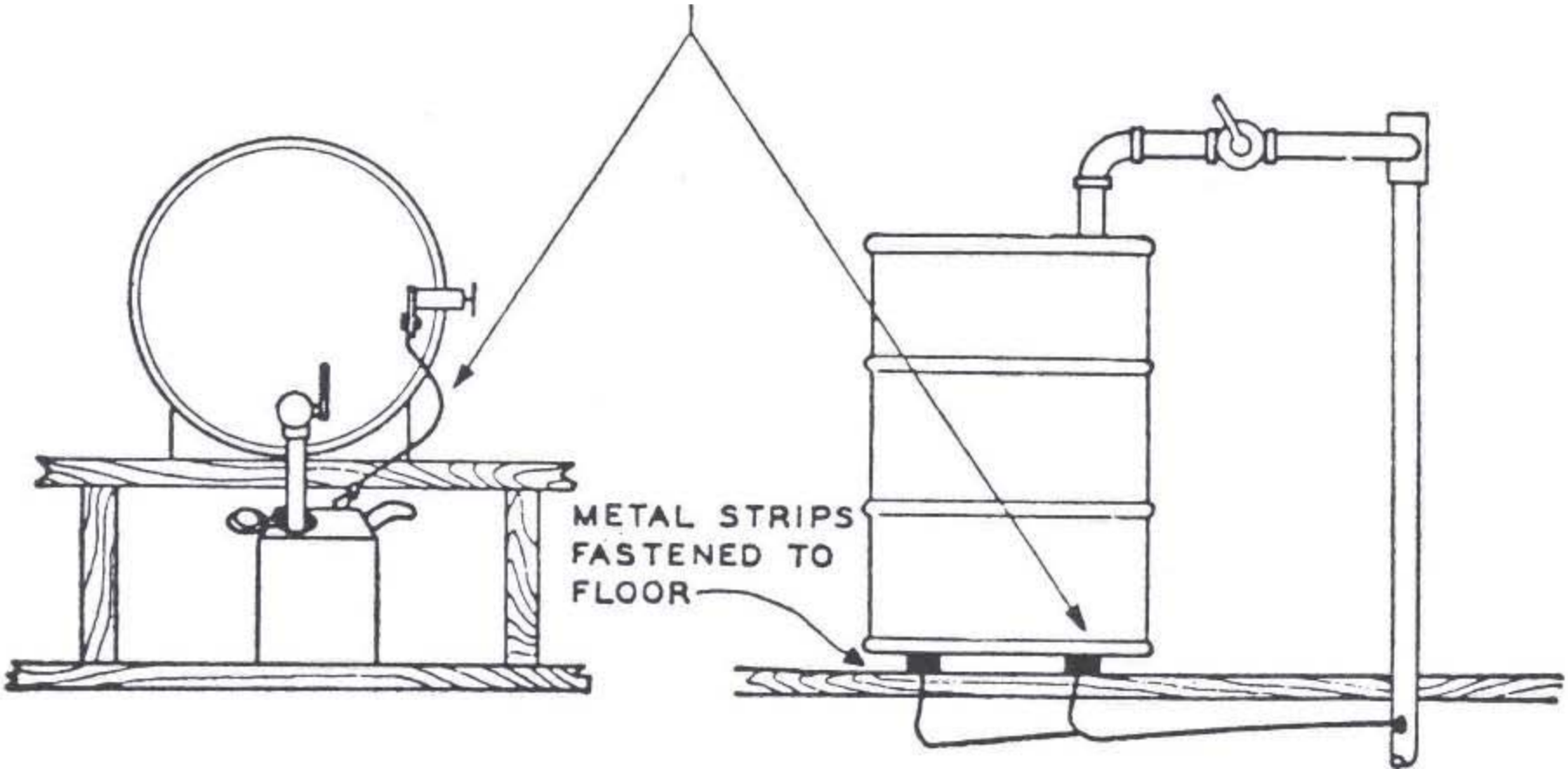
- Use container in a container concept
- Label all containers
- Inform driver of hazards
- Provide contact names, phone numbers
- Provide MSDS

Transfer Chemicals Properly

- **Some flammable liquids accumulate a static electric charge, which can release a spark that ignites the liquid**
- **Always bond metal dispensing and receiving containers together *before* pouring**

Control of Static

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



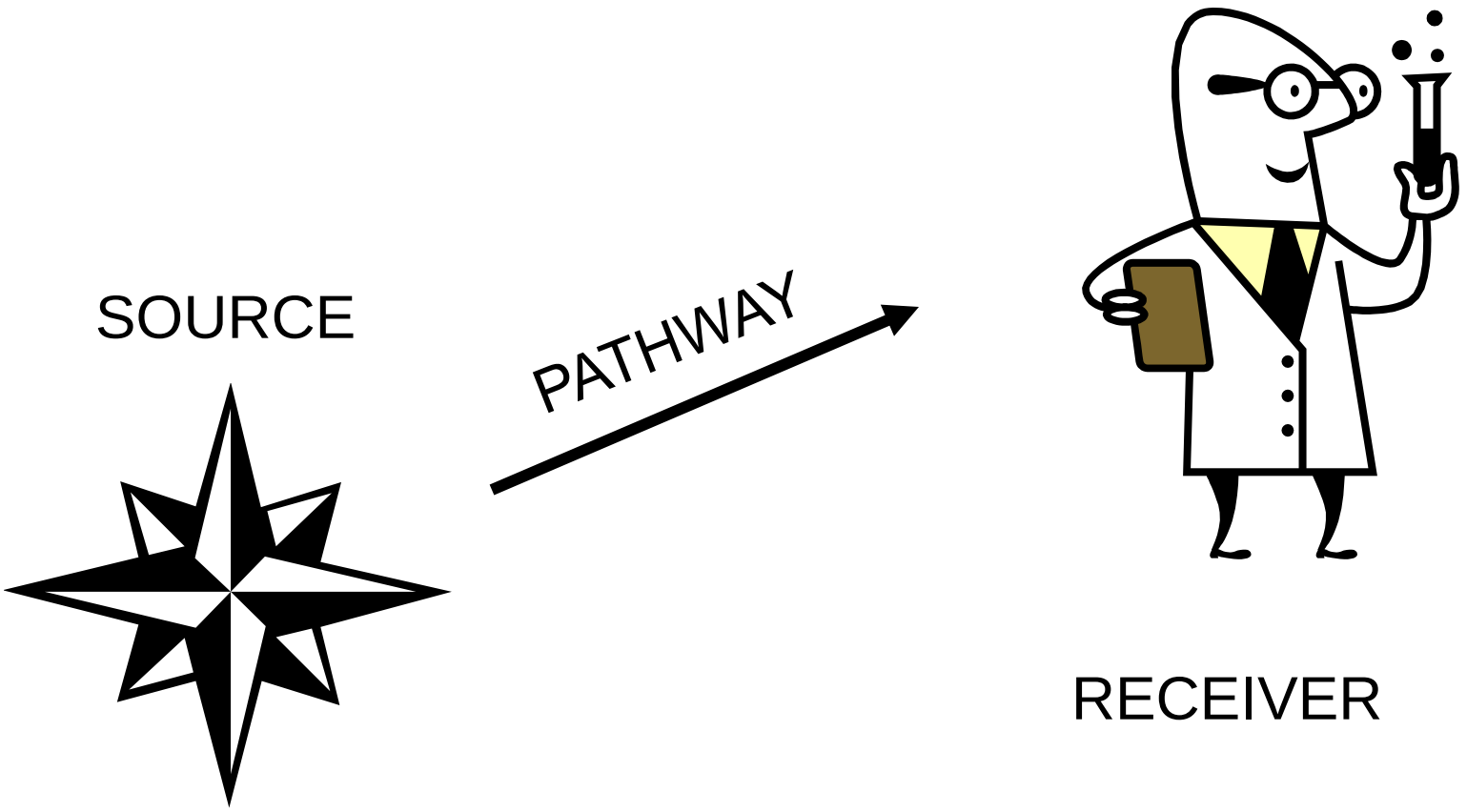
Safe Laboratory Procedures

Housekeeping:

- label all containers
- clean-up spills
- eliminate trips hazards
- proper storage

Dangerous Housekeeping

Engineering Controls



Laboratory Containment Principles

Concept

Source → **Path** → **Receiver**

Control Used

Engineering Control → **Operational Practices** → **PPE**

Engineering Controls

1. Change the process

eliminate the hazard

2. Substitution

non-hazardous substance for hazardous

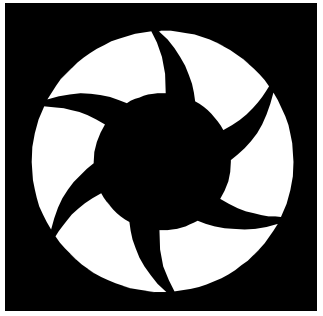
(e.g. - toluene for benzene)

Engineering Controls

3. Isolate or enclose the process or worker

Use a barrier

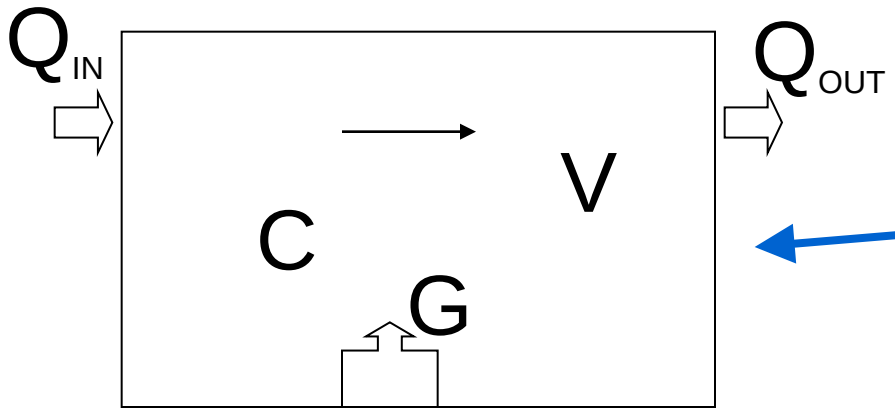
4. Ventilation



Dilution (general ventilation) - Not good

Local exhaust ventilation (LEV) - Preferred

Engineering Controls



Dilution (general) ventilation

not good

Local exhaust ventilation

preferred

Q = flux, C = contaminant conc.
V = velocity, G = generation rate

Engineering Controls

Properly functioning & used correctly!

Laboratory hoods and ventilation are the basis of engineering controls.

Laboratory Hoods

Must be used and maintained properly.

Engineering Controls

Local exhaust ventilation includes:

snorkels

Engineering Controls

Local exhaust ventilation includes: *vented enclosures*

Engineering Controls

Local exhaust includes:

special containment devices

(e.g. - glove boxes)

Engineering Controls

Local exhaust includes:

special containment devices

(e.g. - isolation chambers)

Engineering Controls

Local exhaust includes:

biological safety cabinets

Engineering Controls

- **Special barrier facilities**

  clean rooms, carcinogen rooms, weighing rooms

- **Safety shields**

  radiation shields, hood sashes, splash guards

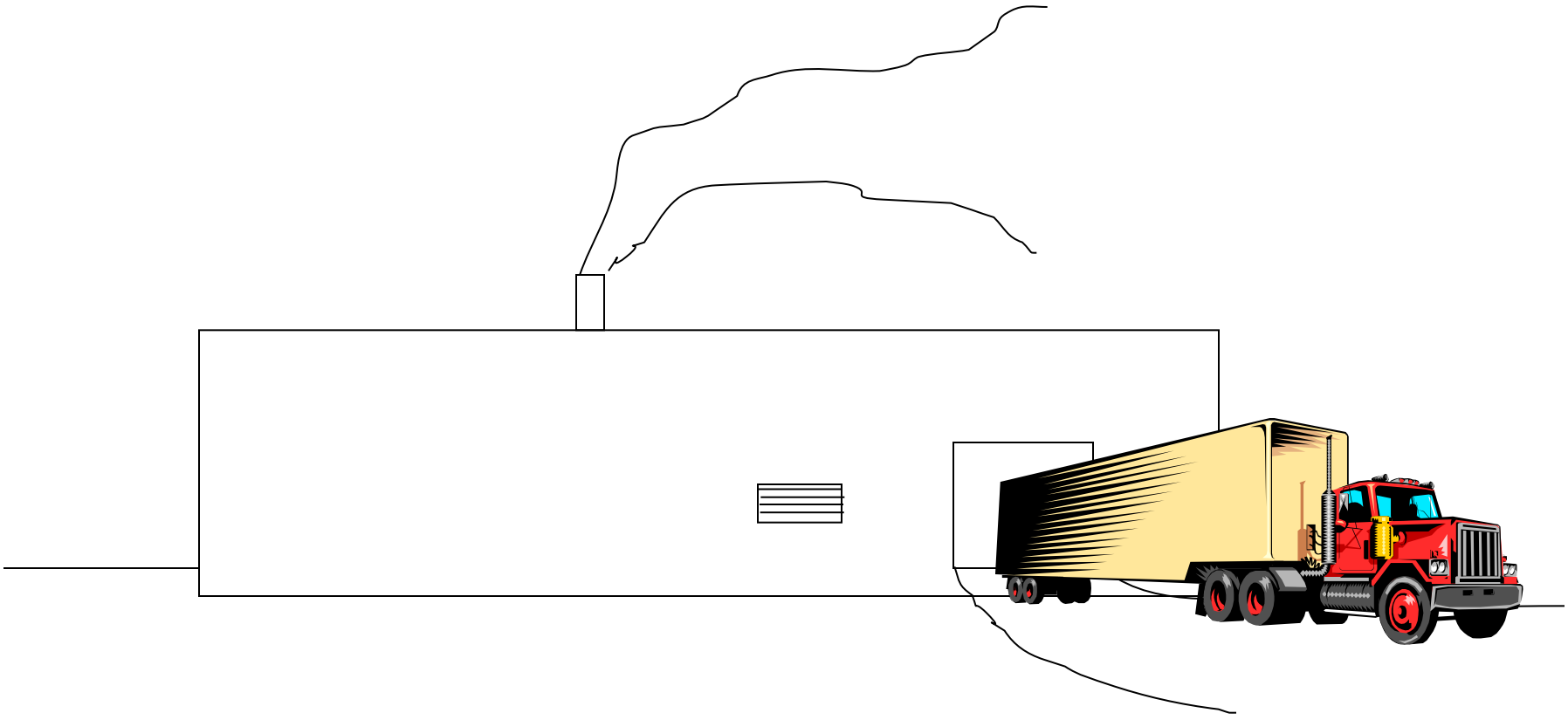
Engineering Controls

Hood exhaust should not be blocked or deflected downward, but should exhaust straight up

Avoid re-entrainment

Disperse emissions straight upward and downwind!

Avoid Recirculation!



Personal Protective Equipment

PPE includes:

eye protection,

gloves,

laboratory coats. etc.,

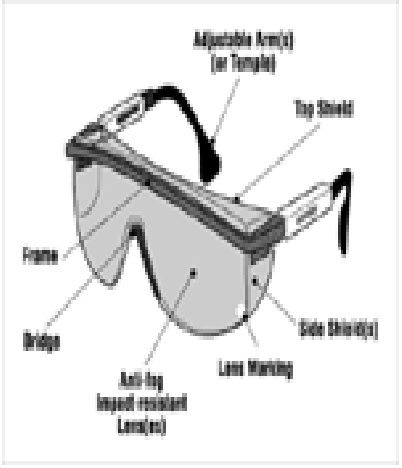
respirators,

appropriate foot protection

Personal Protective Equipment

Eye protection -

specific to the hazard



Personal Protective Equipment

Gloves -

must be chemical specific

Personal Protective Equipment

- Laboratory coats
- Aprons
- Other protective clothing

Personal Protective Equipment
Respiratory Protection

Requires:

training &

fit-testing

Can provide a

false sense of security.

BREAK

Relationships between

Chemical Security

and

Chemical Safety

74

Relationships Between Chemical Safety and Security

- **Chemical safety:** Protect against accidents

- **Chemical security:** Protect against deliberate harm

Many practices are the same for chemical safety and security, but there are a few areas of conflict.

Good Practices for Both Chemical Safety and Security

- **Minimize use of hazardous chemicals.**
  - Replace with less-hazardous chemicals, if possible.
  - Reduce scale of experiments.

- **Minimize supply of hazardous chemicals.**

- **Restrict access to hazardous chemicals.**
  - Know what you have.
  - Know how to store, handle and dispose of what you have.
  - Know who has access to materials, knowledge and expertise.

- **Plan what to do in an emergency.**

Conflicts Between Chemical Safety and Security: Information Sharing

Science generally means sharing information widely, but this may not always be advisable.

- **Safety**
  - Label everything so people can recognize hazardous chemicals.
  - Let community and especially emergency responders know what chemical dangers are there.
  - Share knowledge about chemical hazards so people know to be alert.
- **Security**
  - Labels help identify targets for theft or attack.
  - Sharing locations of chemicals can publicize targets for theft or attack.
  - Sharing knowledge of chemical hazards could inspire harmful behavior (copy-cat criminals).

Conflicts Between Chemical Safety and Security: Facility Exits

- Locking exit doors is secure, but not safe.
  - For safety, people need to be able to leave the facility quickly and by many routes.
  - For security, you want to control exits as well as entrances so chemicals (or equipment) are not taken.

Setting Priorities

- **Labs need to be safe, secure and productive.**
  - Policies and practices need to be flexible enough to allow for the uncertainties of research.
  - Policies and practices need to align with local laws, regulations, practices and culture. Can't just copy from somewhere else.

- **Use risk-based security and safety measures.**
  - Can't afford to defend against every imaginable hazard.
  - Identify threats, characterize facilities, identify alternatives, analyze costs vs. performance.

- **Be alert for suspicious activities or inquiries.**

All Chemical Facilities Need to be Secured

- **Small-scale research laboratories**
  - **Many different chemicals used in small amounts.**

- **Large-scale manufacturing plants**
  - **Limited types of chemicals used in large amounts.**

- **Security measures need to match facility and threat**
  - **Can't afford to defend against all imaginable threat.**

Components of

Chemical Security

81

Chemical Security Questions

- Is your facility secure?
- How easy would it be for someone to steal chemicals?
- Are the chemistry workrooms, stockrooms, classrooms and labs always locked and secure?
- Is someone always there when these rooms are open?
- Do you check your orders when chemicals arrive to be sure some chemicals are not missing?

Components of Chemical Security

- Physical security of site
- Personnel management
- Information security
- Management of chemical security activities
- Allocation of chemical security responsibilities
- Development of emergency plans
- Chemical security training

Goal: Ensure that you don't accidently help a criminal or a terrorist get dangerous chemicals

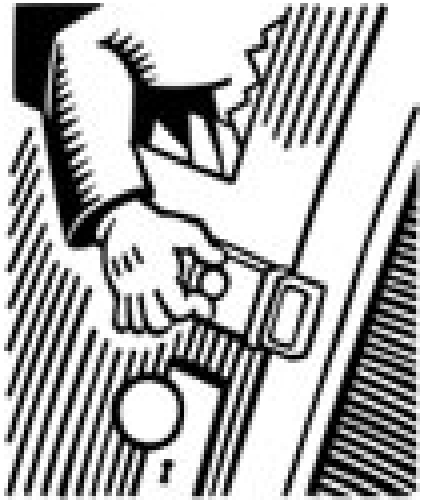
Chemical Security: Physical Site

LOCK UP!!

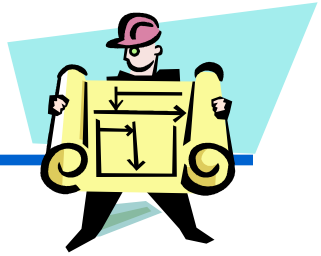
Controlled drugs

Chemical Surety Agents

Highly toxic chemicals



Facility Characterization



Characterize the facility in terms of:

- Site boundary
- Buildings (construction and HVAC systems)
- Room locations
- Access points
- Processes within the facility
- Existing Protection Systems
- Operating conditions (working hours, off-hours, potential emergencies)
- Safety considerations
- Types and numbers of employees
- Legal and regulatory issues

Facility Characterization

Facility characterization provides important data that:

- **Identifies locations and assets to be protected**
- **Establish what existing Protection System components are already present at the facility**
- **Documents facility layout for use in analysis**

Chemical Security:
Personnel Management

- **Guard against both *Insider and Outsider* threat**
- **Who checks people entering the building?**
- **Who has keys? How do they get authorized?**
  - Building
  - Stockroom
  - Individual Labs

- **When someone leaves, do you make sure they turn in keys?**
  - Don't want people making duplicate keys

Threat Definition

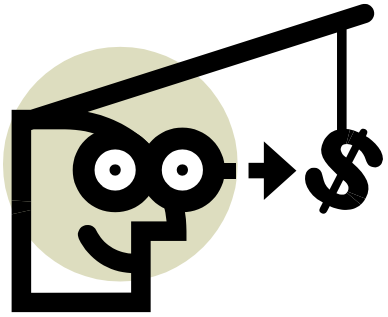
Threat classes:

- Outsiders—no authorized access
- Insiders—authorized access
- Collusion—between Outsiders and Insiders

What Might Motivate Adversaries?

- **Terrorists**
  - Ideology
- **Criminals**
  - Financial
- **Activists**
  - Ideology

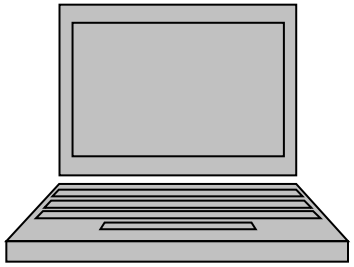
- **Insiders**
  - Ego
  - Ideology
  - Revenge
  - Financial
  - Coercion



Target Identification

- **Determine the possible targets for the following actions:**
  - **Sabotage**
    - **Identify vital areas to protect**
  - **Theft of chemicals**

  - **Theft of information**
    - **Identify location of materials to protect**



Chemical Security: information security

- How do you track chemical inventory?
  - Is the information secured so unauthorized people can't read it or alter it?

- Would you know if:
  - some toxic chemicals disappeared overnight?
  - some toxic chemicals didn't arrive?
  - someone was ordered chemicals in the name of your institution but diverted them?

Chemical Security: Assign Responsibilities

- **Identify people responsible for various chemical security activities:**
  - Physical security, building modifications
  - Chemical tracking and reporting
  - Personnel and access management
  - Information management
  - Emergency planning

- **Ensure they have the time and resources to do the job.**
- **Integrate with chemical safety responsibilities.**

Chemical Security: Professional Behavior

- **Chemical professionals use their scientific knowledge in a responsible manner.**

- **Chemical Educators need to train their students to use their scientific knowledge in a responsible manner.**

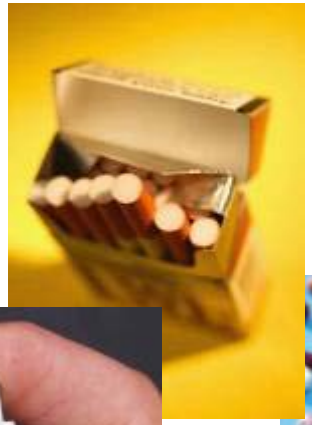
LUNCH

Aspects of Chemical Security

Dual-use Chemicals

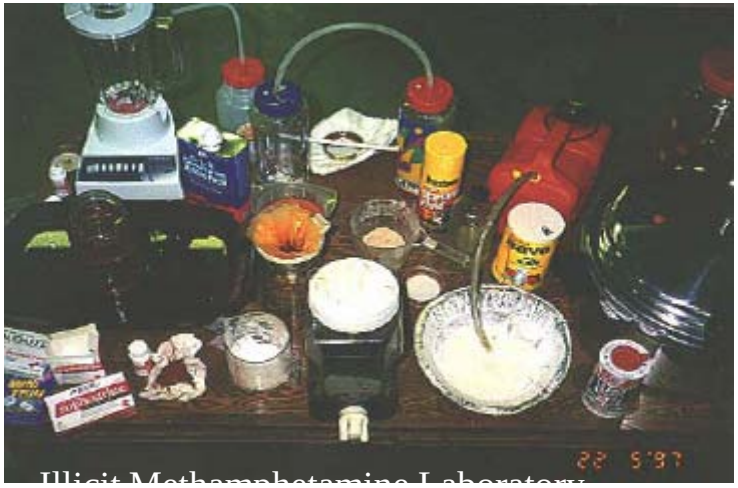
Chemical dual-use awareness

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

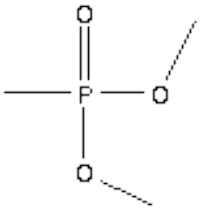
Photo/New York City Poison Control Center

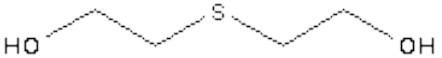
- **Dushuqiang (Strong Rat Poison)**
  - **Outlawed in China in the mid-1980s, but was still available**
  - **Nanjing, China, Sept. 2002**
    - **38 people killed by poison in snack-shop food, >300 sick**
    - **Jealously by rival shop owner**
  - **Hunan, China, Sept. 2003**
    - **241 people poisoned 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**

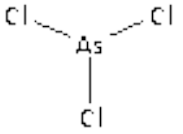
Ann. Emerg. Med., Vol. 45, pg. 609, June 2005

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**



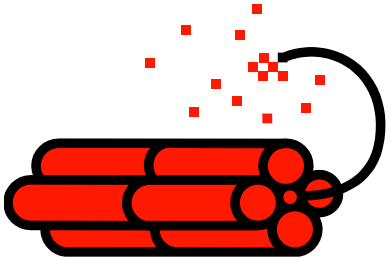




From: Chemical Weapons Convention: Implementation Assistance Programme Manual (on CD)

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



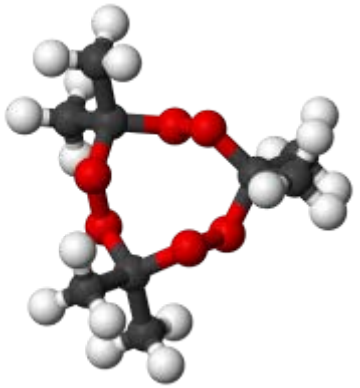
Theft / manufacture of explosives: Fertilizer Bomb

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.

Theft / manufacture of explosives: TATP

- Triacetone triperoxide (TATP)
- Invisible to detectors looking for N-based explosives
- Made using acetone, hydrogen peroxide, strong acid (HCl, sulfuric)
- Favored by terrorists “Mother of Satan”
  - Sept 2009 arrest of N. Zazi, NY and Denver
  - July 2005 London suicide bombs
  - 2001 Richard Reid “shoe bomber”
  - 1997 New York subway suicide bomb plot



CAS 17088-37-8

Wikipedia downloaded Oct 2009
http://en.wikipedia.org/wiki/Acetone_peroxide

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: Bali bombing

- Amrozi purchased chemicals used to make bombs
- One ton of potassium chlorate* purchased in three transactions from the Toko Tidar Kimia fertilizer and industrial chemicals store in Jalan Tidar, Surabaya, owned by Sylvester Tendean.
  - Claimed he was a chemical salesman.
  - Obtained a false receipt saying he purchased sodium benzoate.
  - Tendean lacked proper permit to sell this chemical, didn't know the chemical would be used to make a bomb.
- Details of Aluminum powder purchases not known

* Some press reports state potassium choride, but this is clearly an error

http://www.smh.com.au/articles/2003/06/09/1055010930128.html

http://www.thejakartapost.com/news/2002/12/18/amrozi-owns-possessing-chemicals.html

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

Group Discussion

- **What chemicals are of most concern for diversion?**
  - **Common laboratory/industrial chemicals that would be targeted by someone for illegal reasons such as making explosives, illegal drugs, or chemical weapons.**

International Chemical Controls

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

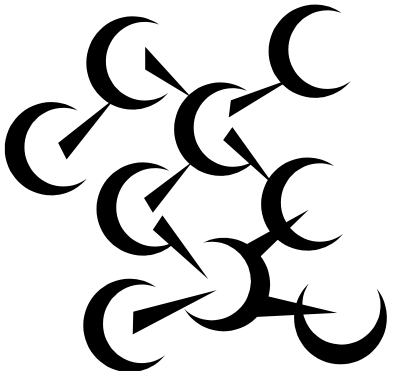
B. Precursors

- (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.**



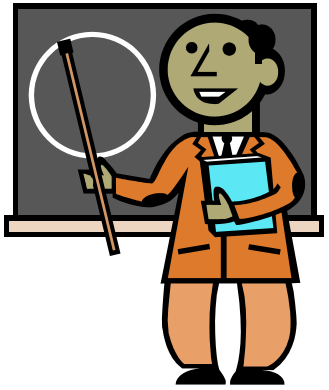
From CWC text – on CD

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.

REACH and the Global Harmonized System for the Labeling of Chemicals

CSP
CHEMICAL SECURITY ENGAGEMENT PROGRAM

Chemical
SAFETY AND SECURITY TRAINING

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://guidance.echa.europa.eu/

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

REACH Help:
http://echa.europa.eu/help_en.asp#helpdesks

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

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

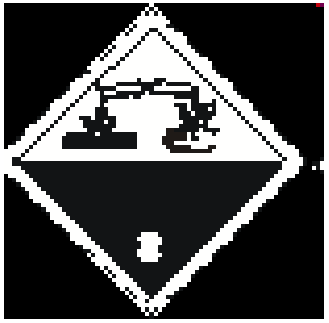
MSDS now named: “SDS” (Safety Data Sheet)

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:



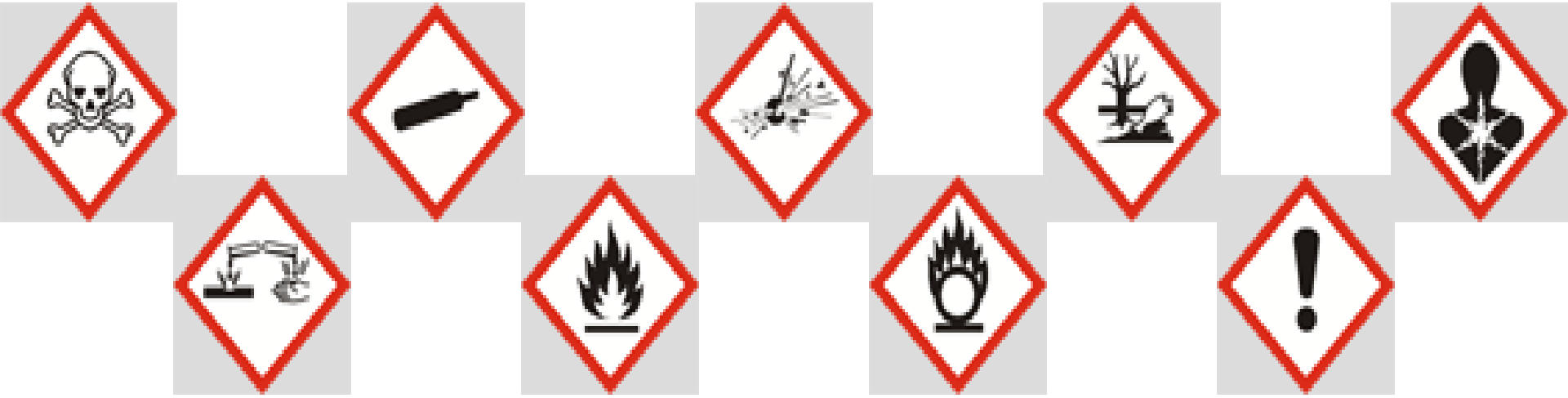
- **Pictograms**
- **Signal words**
- **Hazard statements**
- **Precautionary statements and pictograms**
- **Product identifier**
- **Supplier information**

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/dsg/hazcom/ghs.html

Chemical Safety and Security Plan

First step: Collect information

- **Writing a good CSS plan requires a lot of information**
- **Assessment questionnaires can be used to collect such information**
- **Distribute to:**
  - **PIs**
  - **Management**
  - **Facilities**
  - **Security**
  - **Medical**

Assessment Questionnaire

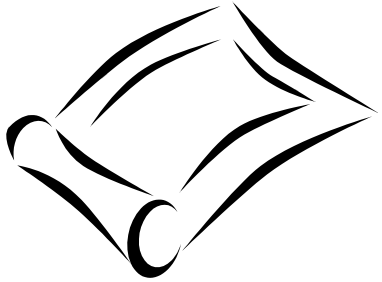
- **Who is responsible for CSS compliance?**
  - Criteria for exposure control
  - Developing exposure control measures
  - Exposure monitoring
  - Identification of hazardous materials
  - Limited access policy
  - Ventilation maintenance
  - Safety equipment
  - Personal protective equipment
  - Training
  - Hazardous waste management
  - Medical surveillance
  - Emergency response

Assessment Questionnaire, cont'd.

- List individuals (managers, PIs, professionals, technicians) with Safety & Security responsibilities; indicate SO, CSSO, BSO, RSO, etc.
- Who maintains CSS records?
- Is there a Safety/Security Committee?
  - Responsibilities
  - Who are the members?
  - How often do they meet?
- Is there a CSS Manual, Plan?
- Are there CSS policies?
- Is there an Emergency Response Plan?
- Are routine CSS inspections conducted?
  - By whom
  - Details

Chemical Safety and Security Plan

- Includes CSS Policy Statements from senior management.
- Describes the entire Program.
- Describes the organization of the Program.
- Explains everyone's responsibilities.
- Describes in general terms policy and who, what, where and why a safety or security task or job is performed.
- Includes references, if necessary.



Parts of a Chemical Safety and Security Plan

- Policy statement from Senior Management
- Safety & Security Organization
  - Management
  - Responsibilities
    - Management
    - Administration
    - CSSO staff
    - Facilities Management
    - Principal Investigators
    - Staff
    - Contractors
- General housekeeping
- Eating, smoking areas
- Signs & labels
- Emergency procedures
- Chemical storage
- Personal protective equipment
- Respirator protective program

Parts of a Chemical Safety and Security Plan, cont'd.

- Engineering Controls
  - Ventilation
  - Laboratory hoods
- Waste Management
- Training
- Record keeping
- Fire Protection & Protection
- Location of emergency equipment
- Evacuation plans
- Personal and environmental monitoring
- Inspections
- Medical surveillance
- Administration
  - Purchasing chemicals
  - Purchasing safety equipment

Standard Operating Procedures (SOP)

- **An SOP explains *concisely and precisely* how, where and who performs a task.**
- **It does *not* explain why the task is done.**
- **The Safety and Security Plan explains policy and why a task is performed**

Standard Operating Procedures (SOP), cont'd.

- **SOPs are:**
  - **Dated**
    - **When issued**
    - **When reviewed**
    - **When revised**
  - **Have: subject, title and identification code**
  - **Officially reviewed by management**
  - **Signed by all responsible parties**
  - **May include forms**
  - **Written in a consistent and official format with numbered pages**

Standard Operating Procedures (SOP)

Consider written SOPs on:

- Security clearance and visitor access
- Employee training
- Medical surveillance
- Respiratory protection and fit
- Eye protection
- Ventilation system maintenance
- Storage, receipt, transport and shipping of hazardous materials
- Accident and emergency response including natural disasters
- Spill cleanup
- Waste management
- Hazardous material handling
- Special operations, radiation, biosafety, lasers, infectious agents

Plan and SOP Revision Guidelines

- **Health and Safety Plan** → **As needed, every 5 years**
- **(M)SDS** → **As received**
- **Laboratory Hoods** → **Quarterly**
- **Training records** → **Yearly, and as needed**
- **Medical Surveillance records** → **As needed, and every 12-18 months**
- **Exposure monitoring**
- **Waste records**

} **As needed**

Record Retention Recommendations

- **Personal records kept by Human Resources for the duration employment + 30 years.**

- **Medical records are *confidential* and should be kept by the examining physician for duration of employment + 30 years.**

- **Most other records (e.g., routine monitoring, should be kept for 5 years after date of performance).**

BREAK

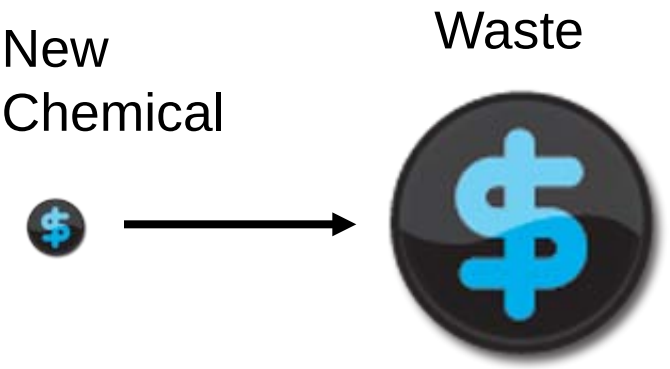
Cradle - to - grave care of chemicals

Receipt → **Storage** →

Use → **Disposal**

Chemical Management is a Best Practice for Safety *and* Security

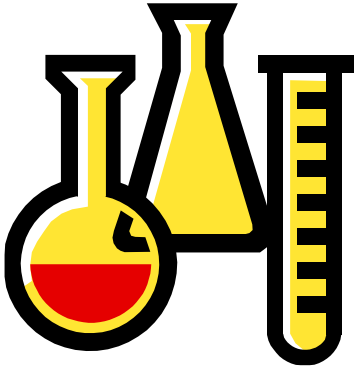
- **Reduces hazardous waste**
- **Reduces cost**
  - **New purchases**
  - **Waste disposal**
  - **More efficient**
- **Improves security**
  - **Insider threat**
  - **Outsider threat**
- **Facilitates environmental compliance**
- **Improves quality of research**
- **Improves quality of lab instruction**



Proper chemical management program has several essential elements

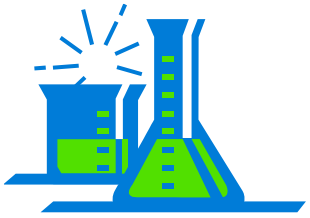
Chemical Management Elements

- Source reduction
- Procedure for chemical ordering and disposal
- Inventory and tracking
- Storage in stockrooms
- Access control
- Recycling of chemicals, containers and packages



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

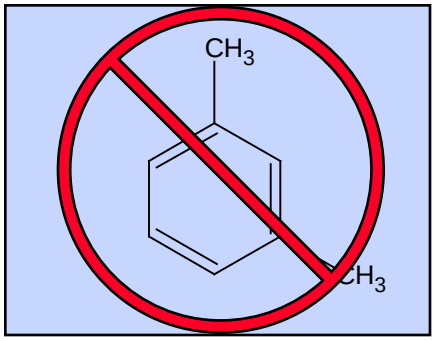
Less is Better !

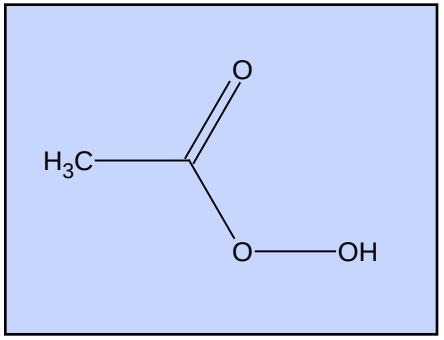
- Order only what you need
- Reduce size of experiment
- It costs less to store
- It costs less to dispose

"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

Substitute reagents to reduce waste

- Citrus based solvents for xylene in histology lab
- Peracetic acid for formaldehyde for cleaning kidney dialysis machines
- Non mercury thermometers
- Enzyme and peroxide based cleaners for chromerge (NoChromix)
- When purchasing automated equipment think of chemical waste





Best practice - ordering and stocking chemicals

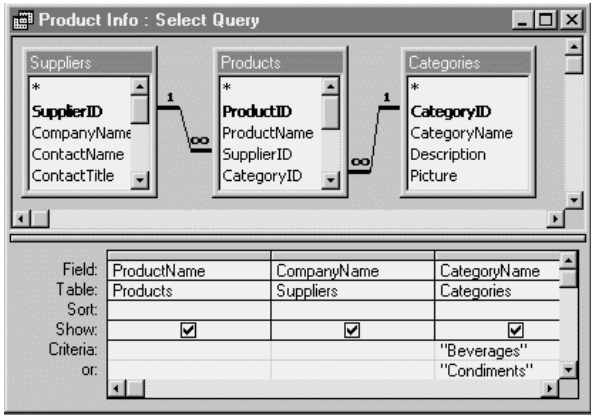
- See if your institution already has it (surplus)
- Order minimum needed (large quantities are not a bargain)
- Check on special storage (refrigeration, dry box…)
- Mark the receipt /open date (unstable chemical)
- Can it eventually be disposed of (rad waste, mixed waste)

Ordering chemicals- chemical inventory

- **Database or Spreadsheets are tools to track the chemical inventory**
  - **Barcoding can be used**
  - **Chemicals can be found easily**
  - **Chemical ages can be tracked**
  - **Chemical standards maintain traceability**
  - **Disposal can be documented**
- **Physical reconciliation**
  - **Assures accuracy of database**
  - **Provides visual inspection of chemical condition**

Inventory and tracking

Database or spreadsheet designs



Home made – Access or Excel programs

Freeware – Based on Access or Excel

Commercial – Chemicals and MSDS included

Database helps safely track and report chemical storage and use

Searches and Reports:

- Find an (M)SDS
- Chemical Inventory Search Menu
- Chemical Regulatory Reports Search Menu
- Find Chemical Storage Locations

Transfers, Removal, Verification and Inventory Entry:

- Transfer or Remove a Bar-coded Chemical from the Inventory
- Verify Chemical Inventory Menu
- Add Chemical Inventory
- Chemical Exchange Menu

Procedures, Forms and Links:

- See Inventory procedures, forms and other documents
- See Other Chemical Related Links

Inventory queries

Chemical or tradename search

CAS number search

Ingredient search

Location/organization search

Location owner search

Requester search

Barcode search

Query result for toluene – barcode, location, department, quantity and order date

BARCODE	LOCATION	DEPT	QUANTITY	UNIT	Purchase Date
AQ00600682	NM/518/1111	1725	1	L	10/24/2006
AQ00602185	NM/518/1123	1111	100	mL	11/20/2006
AQ00582298	NM/518/1302	1131	1	L	8/8/2006
AQ00602186	NM/518/1302	1131	100	mL	11/20/2006
AQ00602187	NM/518/1302	1131	100	mL	11/20/2006
AQ00582307	NM/518/1302	1131	4	L	8/8/2006

(M)SDS and Certificates of Analysis may also be included

Chemicals likely to be useful in other labs

ACIDS

Acetic acid (glacial)
Hydrochloric acid
Sulfuric acid

SOLVENTS

Dichloromethane (methylene chloride), Acetone Chloroform, Ethyl acetate, Glycerol, Hexanes Isopropyl alcohol, Methanol, Petroleum ether Toluene, Xylenes

OXIDIZERS

Bromine, Potassium chlorate, Potassium dichromate, Silver nitrate

POISONS

Indicators, Iodine (solid or solution) Metals (powders, dust, shot)
Sodium, calcium, silver, and potassium salts

Excess chemicals are made available to others and can be searched

CHEMICAL NAME	MSDS	QTY	STATE	PURCHASE DATE	OPEN?
DEVCON 5 MINUTE EPOXY KIT	NL203800	2.5 OZ	Liquid	07/25/2001	Not Open
5 MINUTE EPOXY KIT	NL203800	2.5 OZ	Liquid	08/06/2003	Not Open
TOLUENE	OHS23590	500.0 ML	Liquid	03/25/1999	Not Open
TOLUENE	OHS23590	500.0 ML	Liquid	03/25/1999	Not Open

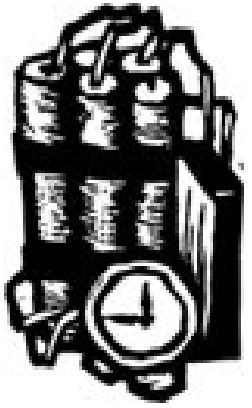
Inventory management

Less is Better !

It's Safer!

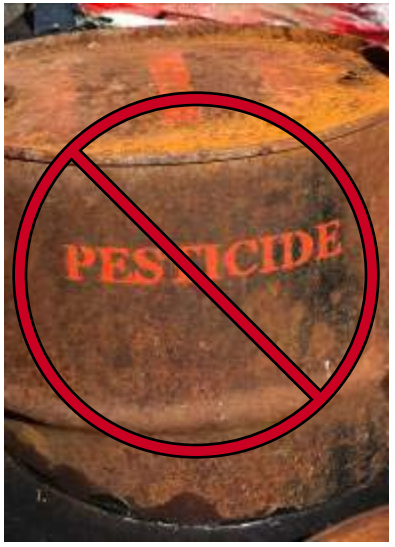
It may be cheaper to order diethyl ether in large containers

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



Inventory management – chemical aging

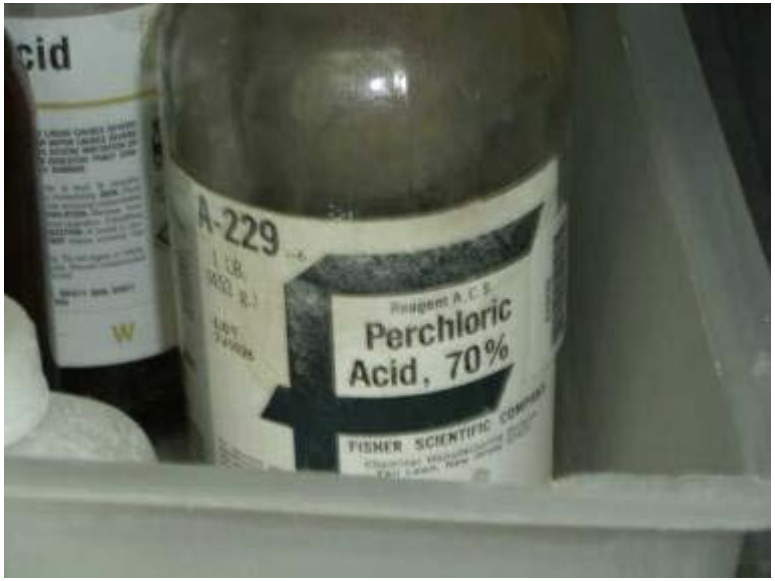
- How old are your chemicals?
- Some chemicals degrade over time
  - rotate stock
  - label & date
- Chemical assays have expiration dates



Explosives and Reactives

Examples:

- Peroxide-forming - ethers
- Perchlorate-forming – perchloric acid
- Water/moisture sensitive – Na, K, Li, LAlH, flammable metals



Control measures:

- Inventory control
- SOPs, inspections

Inventory management

-R-O-O-R-

Peroxide Forming Chemicals

Even with inhibitors they can become dangerous over time

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

Peroxide test kits and strips should be available

Peroxide forming chemicals

- **Peroxide formation is caused by an autoxidation reaction.**
- **The reaction is initiated by light, heat, introduction of a contaminant or the loss of an inhibitor (BHT).**
- **Inhibitors slow, but do not stop peroxide formation.**
- **Most organic peroxide crystals are sensitive to heat, shock, or friction.**
- **It is important not to let peroxide forming chemicals evaporate to dryness or accumulate under screw caps.**

-R-O-O-R-

Peroxide forming chemicals

Peroxides can explode when exposed to thermal or mechanical shock

Examples: ethers, dioxane, tetrahydrofuran

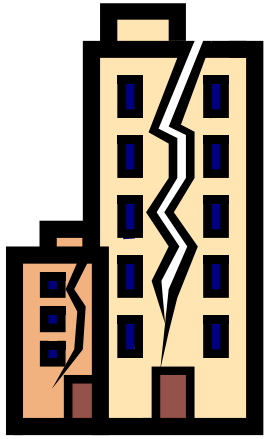
References:

There are excellent websites on peroxide forming chemicals and their hazards, use, storage, and disposal. For example, see:

http://www.med.cornell.edu/ehs/updates/peroxide_formers.htm

Chemical storage

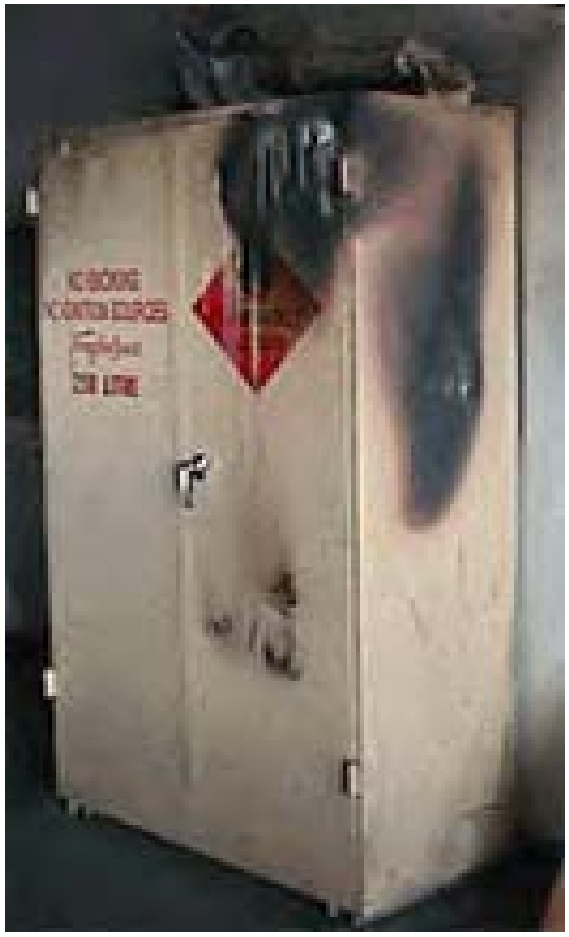
- Protect chemicals during normal operations
- Protect chemicals during unexpected events
  - Floods
  - Tidal waves
  - Earthquakes
  - Typhoons
  - Hurricanes



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

Compressed Gas Cylinders

- Uses
- Types
- Hazards
- Control Measures
  - Inventory control
  - Procurement authorization
  - Training
  - Inspection

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

Damage from Gas-cylinder fire

CSP
CHEMICAL SECURITY
ENGAGEMENT PROGRAM

cal
Y TRAINING

An Accident Waiting to Happen

CSB video: Compressed gas fire

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**

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 safely
  - Preferably use outer protective container

Improper chemical storage

Never use hallways for storage

Safety Hazard!!

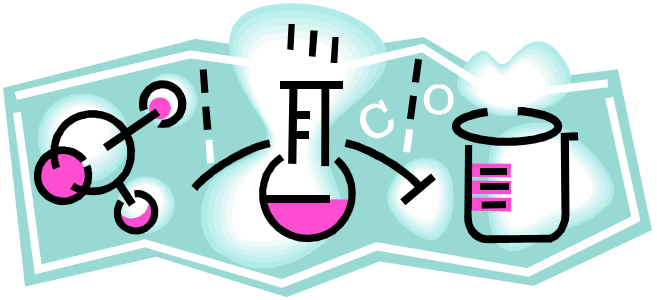
Blocks exit path in emergencies!!!

Chemical storage: Good practices

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

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



From: “School Chemistry Laboratory Safety Guide,” US NIOSH Publication 2007-107

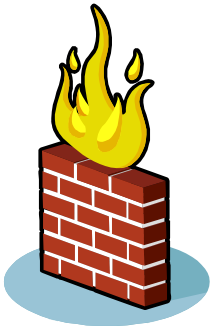
Suggested shelf storage groups: Inorganics

- 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

From: “School Chemistry Laboratory Safety Guide,” US NIOSH Publication 2007-107

Best practice: access control

- Proper training of chemical handling personnel



- Only trained and approved personnel
  - have access to stock room and keys
  - administrative privileges to inventory and database

- Locked doors and cabinets for controlled substances
  - Radioactive materials
  - Drugs and consumable alcohol
  - Explosives (special handling facility)
  - Dual use chemicals
  - Hazardous waste - high toxicity chemicals

References

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

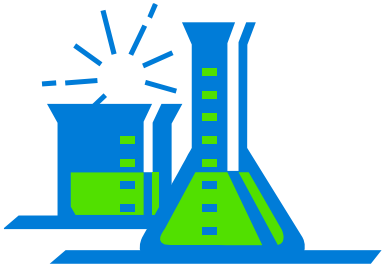
“School Chemistry Laboratory Safety Guide,” US NIOSH Publication 2007-107, Cincinnati, OH, 2006, available on-line: http://www.cpsc.gov/CPSCPUB/PUBS/NIOSH2007107.pdf

“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 Waste Management and Disposal

Waste Management

- Nonhazardous waste
- General guidelines- Storage - Packaging
- Special categories
  - Metal waste
  - Radioactive and mixed waste
  - Biological waste
  - Unknown and orphan waste
- Treat on-site



Waste management: nonhazardous waste

- Used oil (uncontaminated) is not considered hazardous waste. Label Containers "USED OIL", not "hazardous waste."

- Uncontaminated PPE (gloves, wipes)
- Triply rinsed glassware (bottles, droppers, pipettes)
- Salts (KCl, NaCl, Na_2CO_3)

- Sugars - Amino acids
- Inert materials (uncontaminated resins and gels)

Waste management: General guidelines

- Secure and lock waste storage area
- Post signs to warn others
- 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

Waste - Storage guidance

- **Container should not react with the waste being stored (e.g. no hydrofluoric acid in glass).**
- **Similar wastes may be mixed if they are compatible**
- **Whenever possible, *wastes from incompatible hazard classes should not be mixed* (e.g. organic solvents with oxidizers).**
- **Containers must be kept closed except during actual transfers. Do not leave a funnel in a hazardous waste container.**
- **Chemical containers that have been triple-rinsed and air-dried in a ventilated area can be placed in the trash or recycled.**

Waste – General guidance

Certain metals cause disposal problems when mixed with flammable liquids or other organic liquids

Pressure can build up in a waste vessel

Corrosion can occur in storage vessel

Secondary containment is necessary

Glass waste containers can break

Dangerous waste management

Video – Fire at Apex Waste Facility

Best practice – Orphan control

Before moving to new job meet with new lab occupant

- **This can be a new employee or new student**
- **Label all chemicals and samples carefully**
- **Make notations in common lab book**

Dispose of all unneeded or excess chemicals

- **Put into chemical exchange program**
- **Dispose of as hazardous waste**

Do not leave any chemicals behind except by agreement

Waste management

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

Emissions from incineration vs. open burning

	Open Burn (µg/kg)	Municipal Waste Incinerator (µg/kg)
PCDDs	38	0.002
PCDFs	6	0.002
Chlorobenzenes	424150	1.2
PAHs	66035	17
VOCs	4277500	1.2

Source: EPA/600/SR-97/134 March 1998

Laboratory wastes are packaged in small containers

Lab packs consists of small containers of compatible waste, packed in absorbent materials.

Lab packs segregated at hazardous waste facility

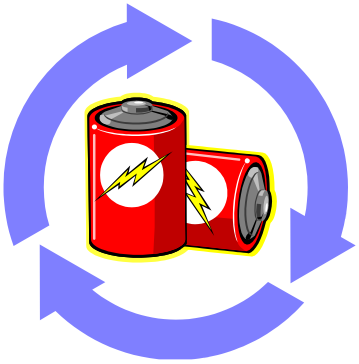
Waste management: Waste disposal service

- 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

Battery recycling and disposal

Hazardous waste

- Lead acid (Pb) - recycle (90% car batteries)
- Sealed lead (Pb) - recycle
- Mercury-oxide (HgO) button, silver-oxide (AgO) button - recycled by jewelers
- Nickel Cadmium (NiCd) recycle



Nonhazardous waste

- Nickel Metal Hydride (Ni-MH) recycle
- Carbon – zinc
- Alkaline
- Zinc-air button

Mercury metal disposal

- Collect pure liquid mercury in a sealable container. Label as "MERCURY FOR RECLAMATION"
- Place broken thermometers and mercury debris in a sturdy sealable plastic bag, plastic or glass jar. Label the container "Hazardous Waste - MERCURY SPILL DEBRIS".
- Never use a regular vacuum to clean up a mercury spill - contaminates vacuum, heat evaporates the mercury
- Never use a broom to clean up mercury – spreads smaller beads - contaminates the broom.

Mixed Waste (chemical radioactive)

These wastes must be minimized - heavily regulated

- **Universities, hospitals**
  - **Low level radioactive with chemical**
    - **Scintillation cocktails**
    - **Gel electrophoresis waste**
- **Nuclear energy research**
  - **Low and high level radioactive with chemical**
  - **Lead contaminated with radioactivity**

Mixed Waste (chemical-biological)

- Medical wastes
  - Blood and tissue
  - Sharps – needles, scalpels
  - Contaminated glassware, ppe
- Autoclave or sterilize
  - Bleach incompatible with autoclave
  - Do not autoclave flammable liquids
- Incinerate

Mixed Waste (radioactive-biological)

Medical wastes

- Often disinfect high biohazard to minimize handling risk
- Let short-lived isotopes decay and then use sanitary sewer
- Refrigerated storage for putrescible waste (carcasses-tissue)
- Autoclave or disinfect labware and treat as low level radioactive
- On-site incineration of low level rad waste if permitted (sharps as well)

Unknown “orphan” waste

Avoid if at all possible -- requires analysis before disposal!

Pre-screen

- Crystals present ? (potential peroxide formation)
- Radioactive (Geiger counter)
- Bio waste? (interview history)

Screen

- Prepare for the worst – wear gloves-goggles-hood

- Air reactivity
- Water reactivity
- Flammability
- Corrosivity

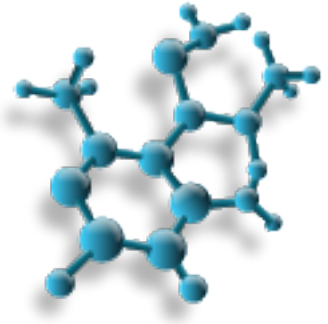
Unknown waste characterization*

Physical description - Water reactivity - Water solubility

pH and neutralization information

Presence of:

- ✓ **Oxidizer**
- ✓ **Sulfides or cyanides**
- ✓ **Halogens**
- ✓ **Radioactive materials**
- ✓ **Biohazards**
- ✓ **Toxics**

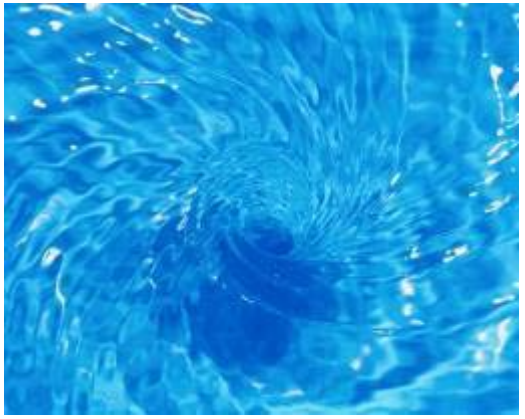


***Prudent Practices in the Laboratory: Handling and Disposal of Chemicals," National Academy Press, 1995 Section 7.B.1**

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**
  - **Check reference books, scientific literature, internet**



Treating on site – volume reduction

Evaporation – if not excessive

- **Roto evaporation for recovery**
- **Do not evaporate corrosives or radioactives**
- **Only in laboratory hood**
- **Beware toxics and flammables**

Adsorption

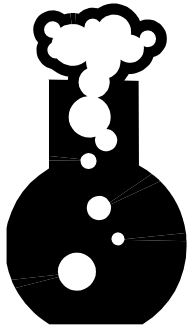
- **Activated carbon**
- **Ion exchange resin**
- **Activated alumina**

Precipitation - Extraction

Handbook of Laboratory Waste Disposal, Martin Pitt and Eva Pitt, 1986. ISBN 0-85312-634-8

Treating on site – chemical conversion

Requires chemical expertise - may not be allowed by regulations - specific to each chemical



Dilution to reduce hazard

- H_2O_2, $HClO_4$, HNO_3
- Never add water to concentrated acid
- Neutralization acid base -gentle

Hydrolysis (acid and base)

- Active halogen compounds with NaOH
- Carboxamides with HCl

Oxidation-reduction

Handbook of Laboratory Waste Disposal, Martin Pitt and Eva Pitt, 1986. ISBN 0-85312-634-8

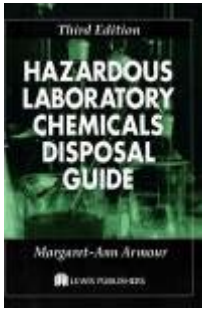
Chemical Waste Example: Tollens Reagent

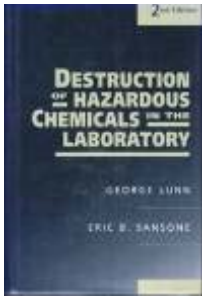
$Ag(NH_3)_2NO_3$ (aq)

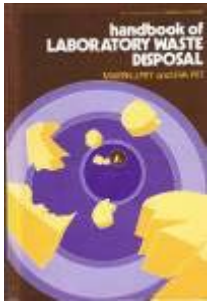
- The reagent should be freshly prepared and stored refrigerated in a dark glass container. It has a shelf-life of ~24 hours when stored in this way.
- After the test has been performed, the resulting mixture should be acidified with dilute acid before disposal. These precautions are to prevent the formation of the highly explosive silver nitride.

Waste management: Treatment in Lab

- **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 Pitt and Eva Pitt, 1986. ISBN 0-85312-634-8**







On-site Recycling and Waste Treatment

Waste Management: Recycling

- Recycling by redistribution
- Recycling of metals
  - Gold-mercury–lead-silver
- Recycling of solvents
  - Clean for reuse-rotovap
  - Distill for purity
- Recycling of oil
- Recycling of E-waste

Chemical recycling

Reuse by others in the organization or community

An active chemical exchange program
- **Beware of accepting unusable chemicals**

Reuse in experiments in the laboratory

Exchange for credit with suppliers by agreement

What should not be recycled

- Gas cylinders past their pressure testing date
- Used disposable pipettes and syringes
- Chemicals and assay kits past their expiration
- Obviously degraded chemicals
- Used tubing, gloves and wipes
- Others?

What should be recycled or redistributed?

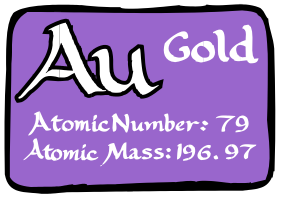
- Excess unopened chemicals
- Excess laboratory glassware (unused or clean)
- Consumables with no expiration
- Solvent that can be purified
    - Lower purity suitable for secondary use?
- Precious or toxic metals
    - Hg, Ag, Pt, Pd, Au, Os, Ir, Rh, Ru
- Others?

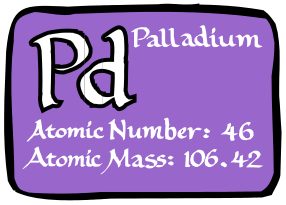
Chemical Recycling - Precious Metal

For reuse in lab or for exchange

- **Requires chemical knowledge for lab reuse**

- **Recover from solution - evaporate then**
  - **Ignite (Au, Pd, Pt)**
  - **Reduce with $NaBH_4$ for metal powder or by electroless plating (Pt, Au, Pd, Ag, Rh).**
  - **Electroplate**
  - **Metal recovery Ion exchange-then ash**





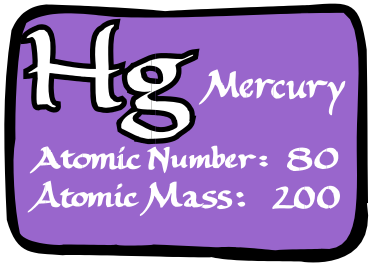
Source : Handbook of Laboratory Waste Disposal, Pitt &Pitt, John Wiley, 1986

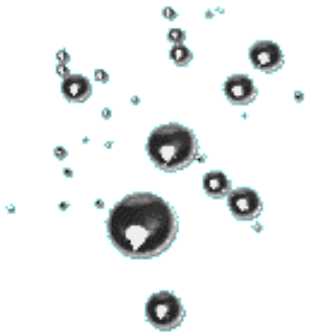
Chemical Recycling - Silver

- **Recovery from chemical oxygen demand (COD) test**
  - **Acidification and ppt as AgCl**
- **Recovery from photographic fixing solution**
  - **Precipitate as sulfide**
  - **Precipitate with TMT (trimercapto-s-triazine)**
  - **Electrolysis (terminal and in-line)**
  - **Metal replacement (iron containing cartridges)**
  - **Ion exchange**
- **Many companies will buy the recovered silver**

Chemical Recycling - Mercury

- Mercury can be recovered for subsequent lab use or for recycle by vendor
- Remove particulates and moisture by allowing slow drip through a hole in a conical filter paper
- Never distill Hg on-site





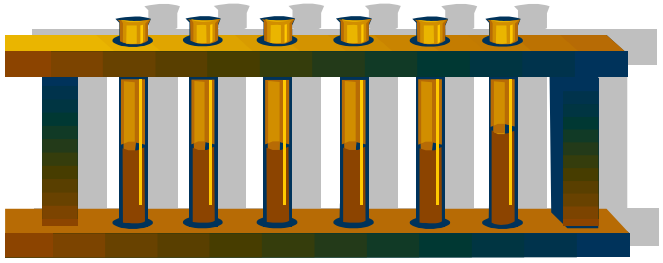
Solvents can be recovered by distillation

- Boiling point must be widely different
- Azeotropes may prevent separation
- Sometimes hazards are created
- Some solvents do not need complete separation
- Hardware for separation

Solvent recycling – general guidance

Solvent recycling requires care and organization

- Keep solvents segregated prior to separation (single product solvent)
- No unnecessary dirt due to careless handling
- Requires good labeling
- A small amount of the wrong chemical can ruin a desired separation
- Care must be taken not to concentrate peroxides



Solvent recycling – general guidance

Solvent recycling requires care and organization

- Try other purification methods before distillation
  - Convert to precipitate
  - Convert to water soluble
  - Use an adsorbent
- Need BP difference of > 10°C
- Can form azeotrope*
  - water / ethanol (100°C/ 78.3°C)
  - cyclohexane / isobutanol (81°C / 108°C)
- Mixture of 4 solvents not practical
- Distillation can be incorporated into curriculum

* Consult CRC Handbook of Chemistry and Physics for list of azeotropes

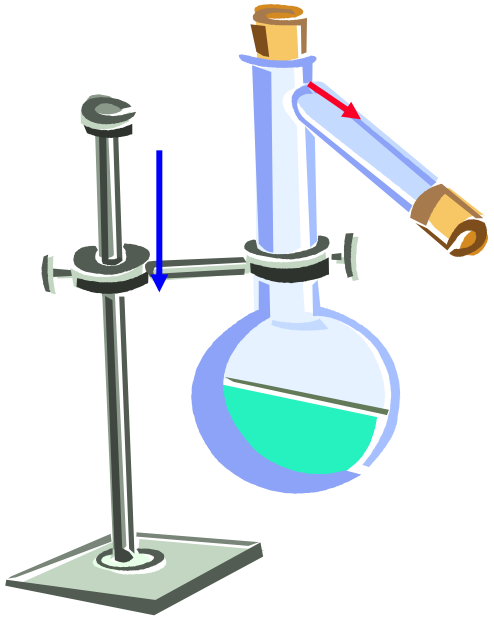
Solvent recycling – low efficiency

Rotovap can be used to pretreat

- Toxic material may be kept from the distillation
- May be sufficient if purity is not crucial
- Separation of solvent from solids

Solvent recycling – basics

Reflux ratio	TP
120	25
80	24
40	21
20	16
10	10
4	5



Reflux

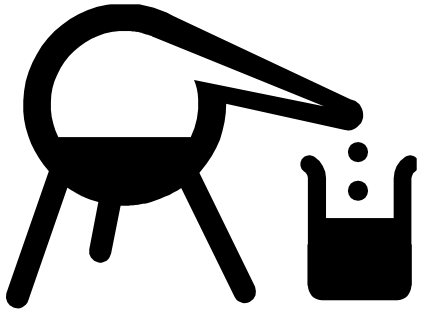
Distillate

Higher reflux ratio leads to increased separation efficiency

TP = theoretical plates

Solvent recycling – medium efficiency

- Even high efficiency stills are not perfect
- Continuous better than batch for large volumes
- Control reflux
- Monitor head temperature
- Reduce heat loss to get more efficiency
- Do not let still operate to dryness
- Use boiling chips but do not add when solvent is hot

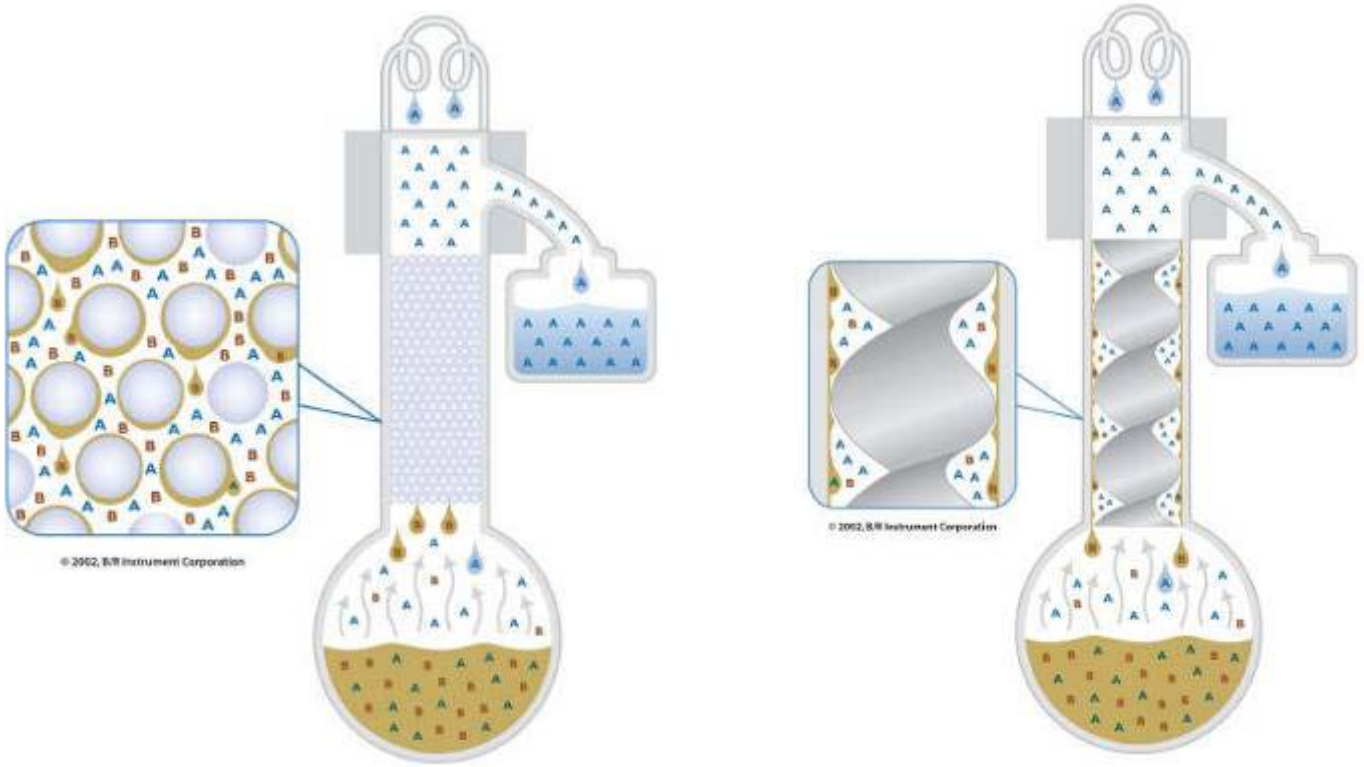


Example: 200mm long column for separating benzene and toluene

Packing	TP
Empty	0.5
Coarse packing	1
Fine packing	5

TP = theoretical plates

Diagram of packed and spinning band distillation columns



Diagrams from B/R Instruments: http://www.brinstrument.com/

Boiling point of common solvents (C)

Halogen Containing		
Dichloromethane	40	CH_2Cl_2
Chloroform	61.6	CH_3Cl
Carbontetrachloride	76.5	CCl_4
Trichloroethane	87	$C_2H_3Cl_3$
Perchloroethylene or Tetrachloroethylene	121	C_2Cl_4
Trichloroethylene	87	C_2HCl_3
Trichlorobenzene (TCB)	208.5	$C_6H_3Cl_3$

Boiling point of common solvents (C)

Oxygen Containing		
Acetone	56.1	C_3H_6O
MEK (Methyl ethyl ketone)	79.6	C_4H_8O
Acetic acid	118.1	$C_2H_4O_2$
Ethyl acetate	77	$C_4H_8O_2$
Ethylene glycol	197	$C_2H_6O_2$
Propylene glycol	187	$C_3H_8O_2$
Ethyl ether	34.5	$C_4H_{10}O$
THF (tetrahydrofuran)	66	C_4H_8O
MIBK (Methyl isobutyl ketone)	116.8	$C_6H_{12}O$

Boiling point of common solvents (C)

Oxygen Containing (cont)		
Methanol	64.5	CH_4O
Ethanol	78.3	C_2H_6O
n-Propanol	97	C_3H_8O
Isopropanol	82.5	C_3H_8O
n-Butanol	117.2	$C_4H_{10}O$
sec-Butanol	99.5	$C_4H_{10}O$

Boiling point of common solvents (°C)

Hydrocarbons		
n-Pentane	36.1	C_5H_{12}
n-Hexane	68.7	C_6H_{14}
Cyclohexane	80.7	C_6H_{12}
n-Heptane	98.4	C_7H_{16}
n-Octane/iso-octane	125.7 / 117.7	C_8H_{18}
Toluene	110	C_7H_8
Ethylbenzene	136.2	C_8H_{10}
p/m/o-Xylene	138.3 / 139.1 / 144.4	C_8H_{10}

Boiling point of common solvents (C)

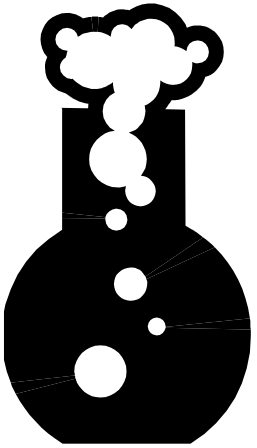
Nitrogen Containing		
Pyridine	115	C_5H_5N
Aniline	184	C_6H_7N
n,n-Dimethylformamide	149-156	C_3H_7NO
n-Methylpyrolidone	202	C_5H_9NO
Piperdine	106	$C_5H_{11}N$
Acetonitrile	81.6	C_2H_3N

Solvents that should not be recycled by distillation

Accidents have been reported for these distillations

Individual Substances

- Di-isopropyl ether (isopropyl alcohol)
- Nitromethane
- Tetrahydrofuran
- Vinylidene chloride (1,1 dichloroethylene)

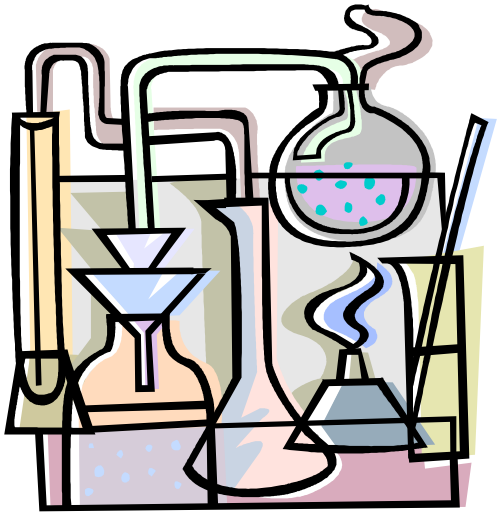


Mixtures

- Chloroform + acetone
- Any ether + any ketone
- Isopropyl alcohol + any ketone
- Any nitro compound + any amine

Practical examples of recycling

- **Hexane contaminated with small amount of inert solvent used in prep lab**
- **Chemistry students given a finite quantity of solvent, then had to recycle for subsequent experiments**
- **Acetone 50% in water for washing. Azeotrope is 88.5% which is then diluted back with water for reuse**
- **Use rotovap recovery rather than evaporation. Student will redistill; 60% recovery.**
- **Third wash was captured and used as first wash on next experiment**



Source : Handbook of Laboratory Waste Disposal, 1986.
Marion Pitt and Eva Pitt, John Wiley and Sons, ISBN 85312-634-8

Solvent recycling

Automated systems help with large needs

HPLC Solvent Recycling

GPC Solvent Recycling

Environmental Laboratory Solvent Recycling

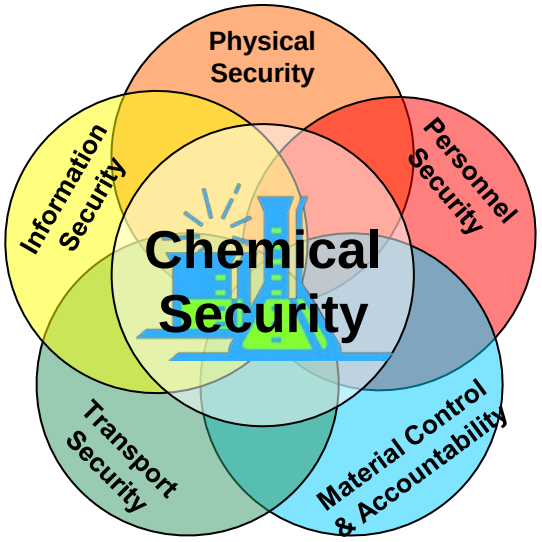
Freon Solvent Recycling

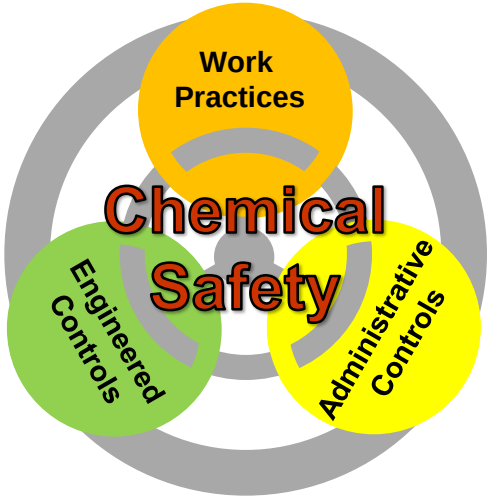
Histology Laboratory Solvent Recycling

General Lab Solvent Recycling Services Can also be Purchased

Pictures from B/R Instruments: http://www.brinstrument.com/

Risk Assessments





Consequences, Mitigations, Prioritization

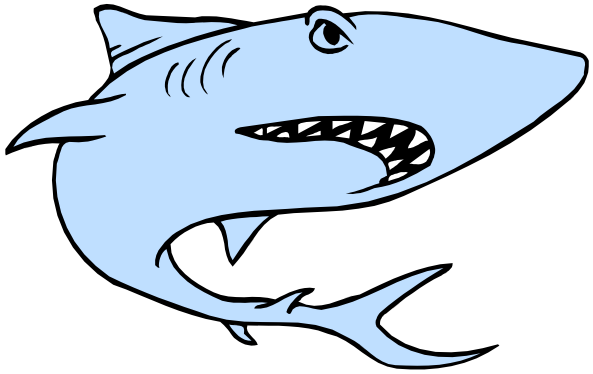
Why Risk Assessment?

- **Laboratory Chemical Safety**
  - **preventive measures designed to reduce the risk of accidental exposure to or release of a chemical hazard**
- **Laboratory Chemical Security**
  - **preventive measures designed to reduce the risk of intentional removal (theft) and misuse of a chemical hazard – intent to cause harm**
- **Identification of preventive measures is determined by the RISK ASSESSMENT**

Risk Governance Strategy

What is a Hazard?

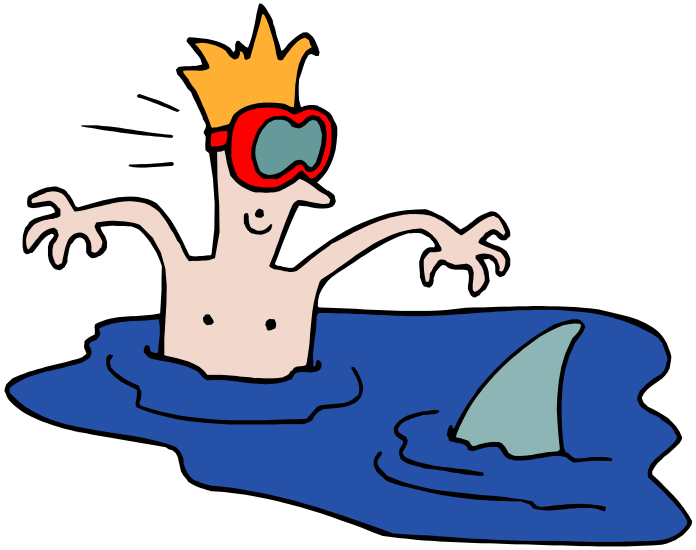
- **Hazard is a source or object that can cause harm**



- **Hazard is *not* a risk without a specific environment or situation**

How do you Determine Risk?

- **Risk is the likelihood of an event that has consequences**



Work activity: Snorkeling

Describe Work Activities:
Snorkeling

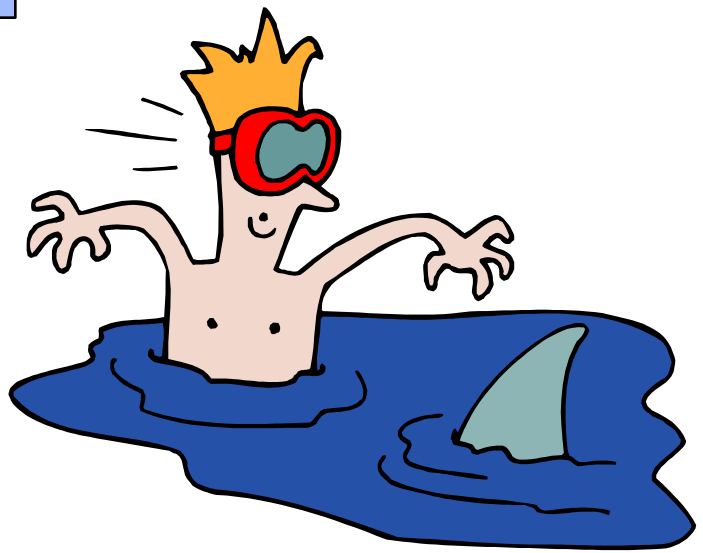
↓

Identify Hazards:
Shark

↓

Determine Risks:
Shark bite, drowning

↓



Work activity: Reactive Chemicals

Describe Work Activities:
mixing reactive chemicals

↓

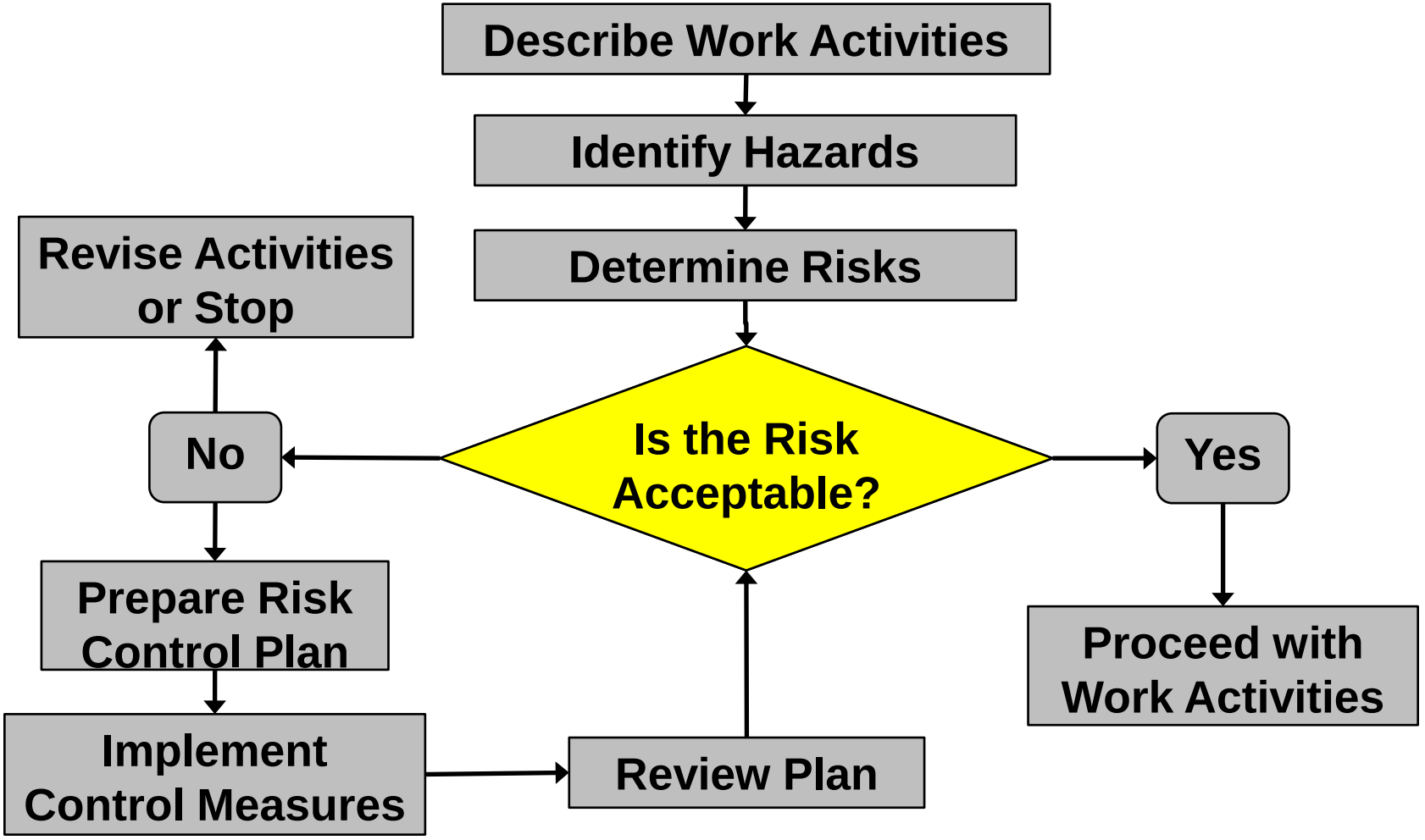
Identify Hazards:
reactive/incompatible chemicals

↓

Determine Risks:
explosion, fire

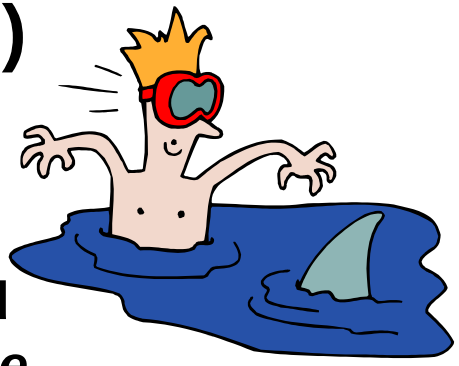
↓

Is The Risk Acceptable?



Is The Risk Acceptable?

Risk = *f* (Likelihood, Consequence)



- **Likelihood**
  - **the probability of harm from a given hazard and the likelihood of exposure *based on the procedures and work practices***
- **Consequences**
  - **degree of harm from accidents**
- **Risks**
  - **exposure to hazard**

Is The Risk Acceptable?

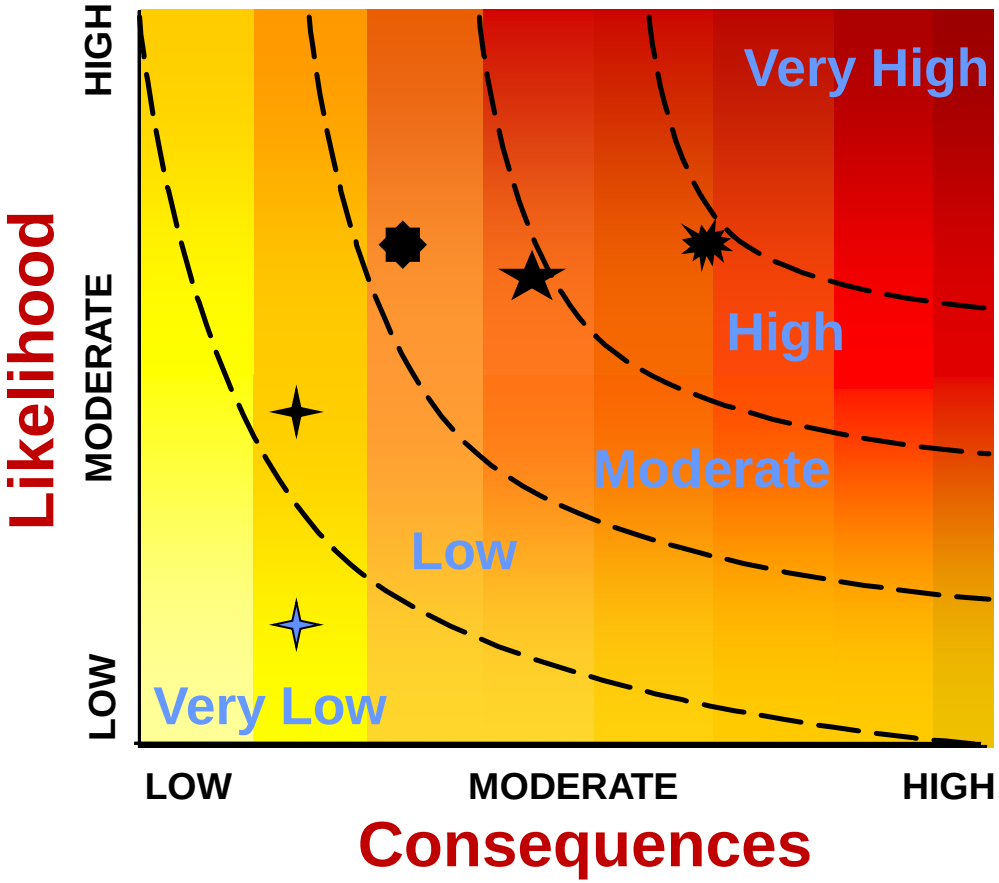
Risk = f (Likelihood, Consequence)

- **Likelihood**
  - **The likelihood of harm by the agent and the likelihood of exposure through an infectious route based on the procedures and work practices**
- **Consequences**
  - **of disease/harm from accidental exposure**
  - **of explosion from reaction**
  - **of fire from heat/spark**
- **Risks**
  - **accidental exposure to laboratory workers**
  - **accidental exposure to community**
  - **accidental exposure to environment**

Risk Evaluation

- **Value-based judgement:**
  - what is acceptable,
  - what is tolerable,
  - what is intolerable?

- **Based on:**
  - consequence:
    - severity of harm/damage?
  - likelihood:
    - frequency of exposure?



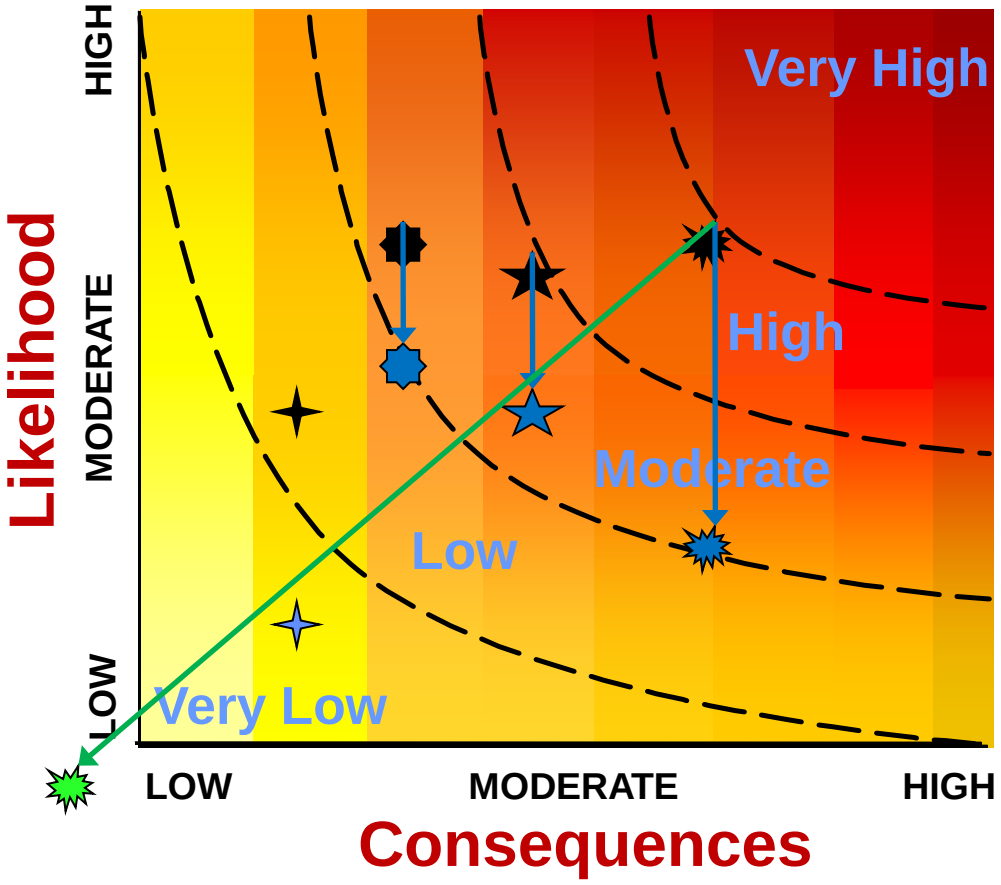
Risk Evaluation

- Identify factors that influence likelihood:
  - for each risk
  - what are routes of exposure?
  - what engineered controls are in place?
  - what work practices are expected?

- Identify factors that influence consequences:
  - for each risk
  - what harm/damage may occur?
  - how severe of a consequence?
  - harm and damage to whom?
- Is the risk high, moderate, or low?
  - why?
  - can it be reduced?

Risk Evaluation for Risk Reduction

- **Reducing risk:**
  - **can we eliminate hazard?**
  - **can we reduce likelihood?**
- **Risk-hazard reduction:**
  - **eliminating hazard *WILL* eliminate risk**
    - **best strategy**
    - **may not be possible**
  - **reducing hazard *MAY* reduce risk**
    - **good strategy**
    - **may be best option**



Risk Evaluation

What would be **different** if the activity was a laboratory's work or chemicals being stolen?

by an outsider?

by an outsider with insider help?

Does the hazard change?
Does the risk change?
To whom?

Hazard, Threat and Risk

- A **hazard** is a source or object that can cause harm

- *A **threat** is a person who has intent to cause harm to other people, the community, the environment, or the institution*

- A **risk** can be based on either a hazard, or a hazard and a threat

Is The Risk or Threat Acceptable?

Chemical Security Assessment

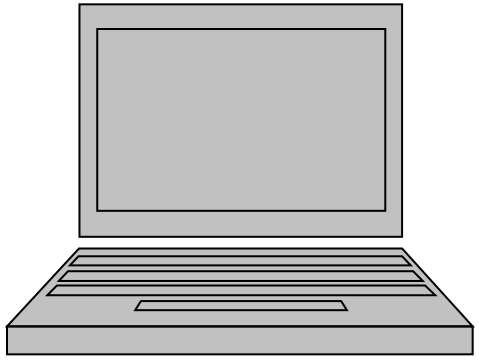
1. **Characterize chemicals and threats**
   a. evaluate chemical compounds at a facility (Asset Assessment)
   b. evaluate adversaries who might attempt to steal those chemicals or equipment (Threat Assessment)

2. **Characterize the facility**
   a. evaluate the likelihood the facility will be targeted
   b. evaluate the likelihood of a successful theft (Vulnerability Assessment)

3. **Characterize the risk**
   a. evaluate the overall likelihood and consequences of each scenario
   b. determine acceptable and unacceptable risks; develop risk statement

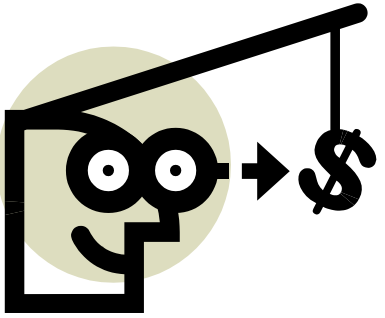
Characterize Chemicals (Assets)

- **Chemical Properties:**
  - **flammability**
  - **vapor pressure**
  - **toxicity**
  - **routes of exposure**
  - **environmental hazard**
- **Equipment:**
  - **special uses (unique)**
  - **expensive/hard to purchase**
- **Availability:**
  - **sources**
  - **waste disposal/treatment**
  - **transportability**
  - **identifiable**



Characterize Threats

- **Possible adversaries:**
  - **criminals**
    - **use for drugs**
    - **sell to others**
  - **terrorists**
  - **extremists**
  - **angry worker/employee**
- **Motivations:**
  - **profit / money**
  - **social and economic disruption**
  - **malicious damage/revenge**
  - **ideology**

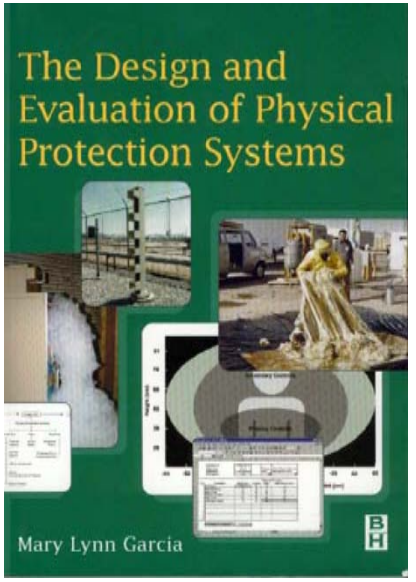


Characterize Facilities

- **Characterize the facility considering:**
  - **mission**
  - **operations**
  - **budget**
  - **safety**
  - **legal issues**
  - **regulatory issues**

Characterize Facilities

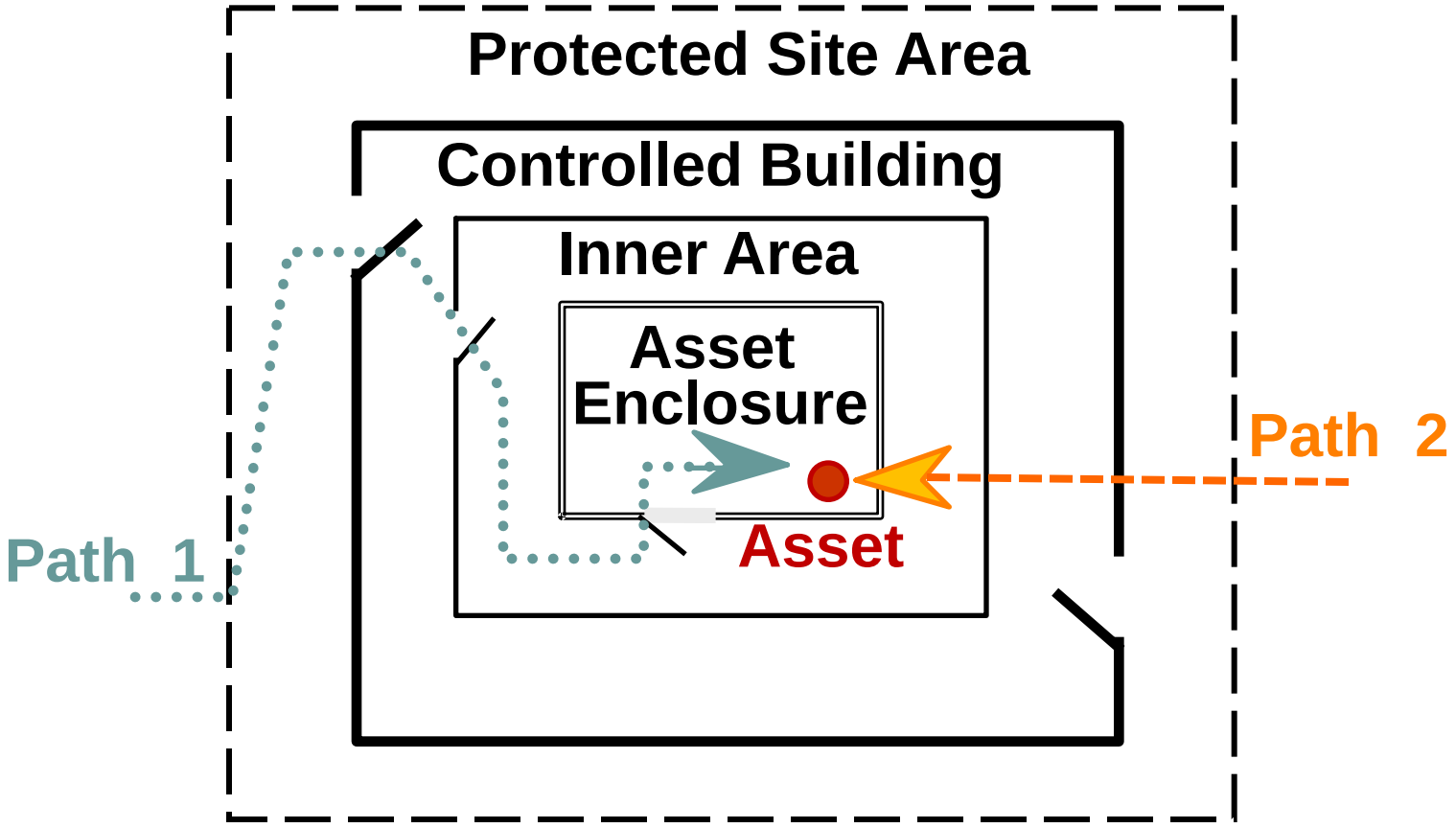
- **Characterize the facility in terms of:**
  - site boundary
  - buildings (construction and HVAC systems)
  - room locations
  - access points
  - processes within the facility
  - existing protection systems
  - operating conditions (working hours, off-hours, potential emergencies)
  - safety considerations
  - types and numbers of employees



Characterize Facilities

- Facility access control:
  - site controls
  - keyed building access
    - key issuing and controls
    - electronic monitoring
  - guard stations
    - detection, assessment and response
- Chemical/equipment protection:
  - locked cabinets for chemicals of concern
  - computer access controls (passwords, etc)
  - inventory tracking
  - equipment/chemical ownership/responsibility
  - procurement approvals required

Characterize Facilities: Adversary Paths to Asset

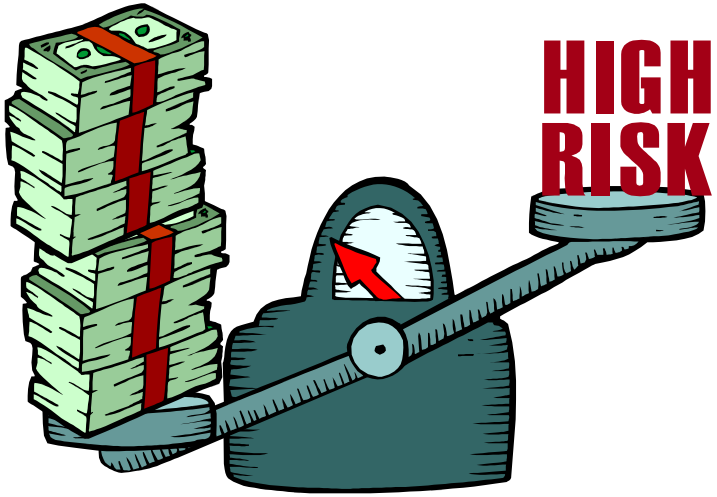


Characterize exposure/release consequences

- **Health consequences:**
  - **disease**
  - **mortality**
  - **burns, etc**
- **Property damage:**
  - **fire losses**
  - **explosion damage**
  - **contamination losses**
- **Community & Environment:**
  - **social disruption**
  - **resource loss/damage**
  - **economic consequences**

The Main Question

- How much risk is acceptable versus the cost of reducing that risk?
- Must manage multiple risks in a holistic manner
  - financial
  - liability
  - health and safety
  - business/mission
  - security



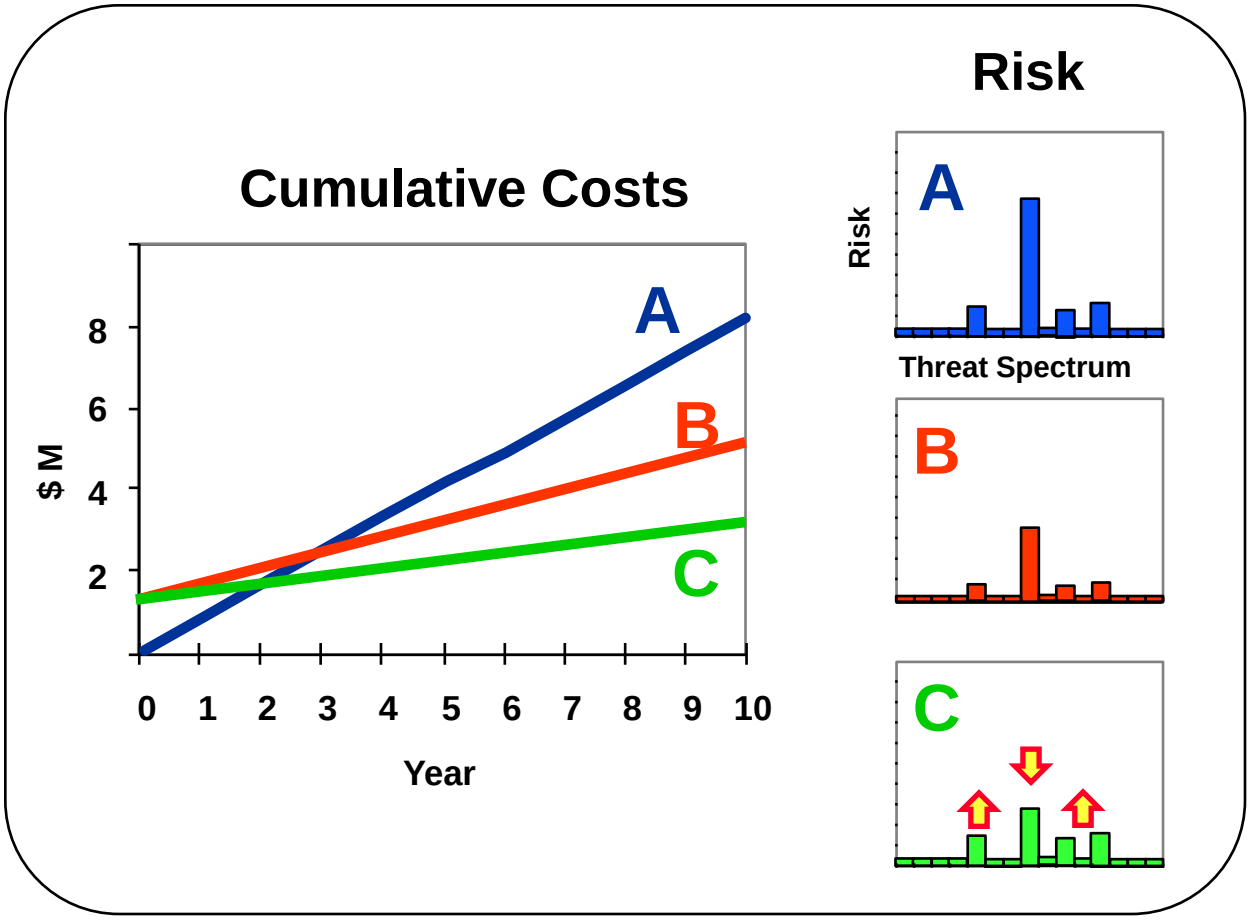
Chemical Security and Risk/Threat Prioritization

- Same concepts as Safety Risk Evaluation:
  - likelihood of theft/misuse
  - consequence of intentional misuse
  - must now consider the adversary
- Value judgement:
  - what is acceptable, tolerable, unacceptable?
- Controls & Mitigation:
  - facility access
  - education and training
  - employee screening
  - site/facility monitoring
  - security personnel
  - emergency response

Chemical Security and Risk/Threat Prioritization

- **Balance of risk and resources:**
  - **consequence versus likelihood**
  - **cost versus performance (risk reduction)**
- **Consider mitigation and prevention steps**
  - **can we afford the loss and damage?**
  - **how do we prevent it?**
  - **can we afford to prevent it?**
- **Lab/institution needs to be productive**
- **Work culture of being alert is best for security *and* safety**

Cost Versus Risk



Risk Assessments: Summary

- Assess the risk by determining likelihood and consequence to allow for strategic decisions on control measures.
- Ideally we consider elimination or substitution first, to remove the hazard.
- A combination of measures might be used based on their effectiveness and our ability to use them and maintain them.
- Cost versus performance (risk reduction)

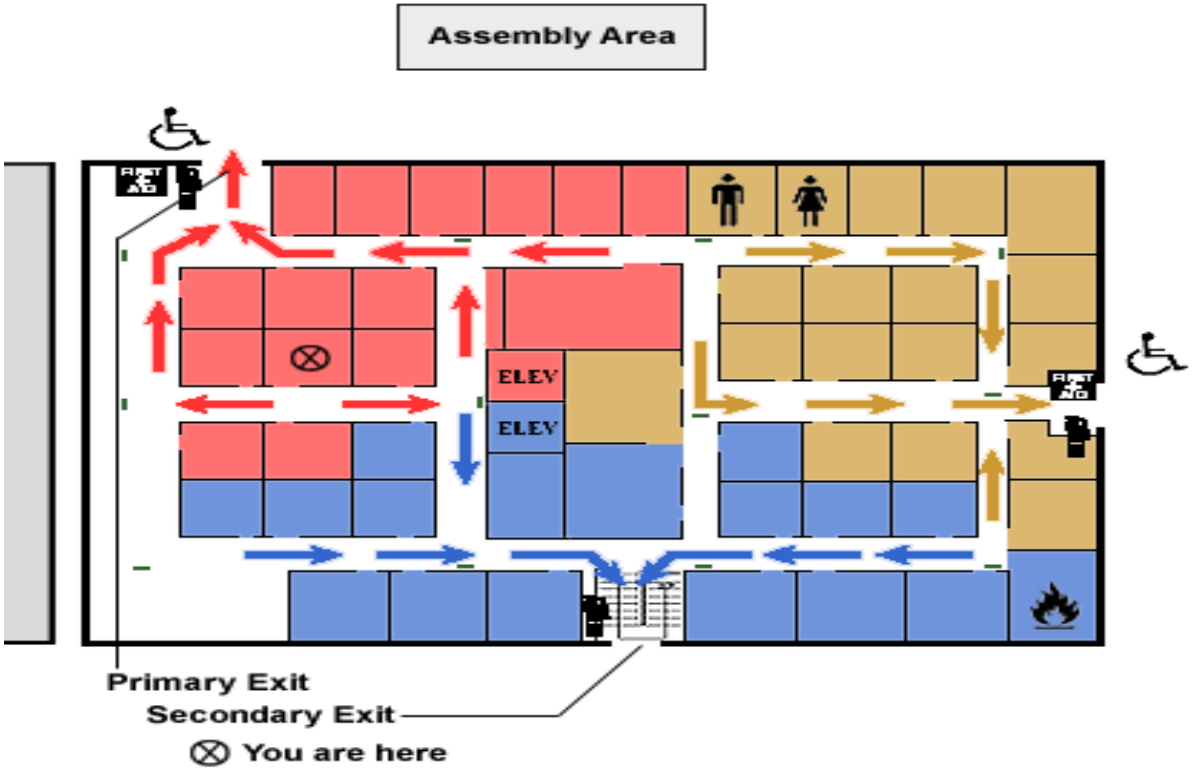
Laboratory Emergency Planning, Response, and Management

CSP
CHEMICAL SECURITY ENGAGEMENT PROGRAM

Chemical
SAFETY AND SECURITY TRAINING

Emergency Planning & Response

Have an evacuation plan and POST IT!



Emergency Planning & Response

Never use hallways for storage

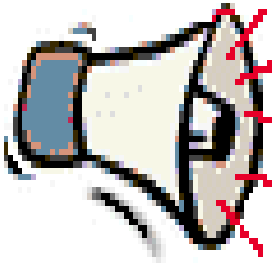
Dangerous!!

Blocks passage and emergency exits

Emergency Planning & Response

- Have routine, unannounced evacuation drills.
- Designate a person for each area to ensure bathrooms, etc. are evacuated.
- Locate outside staging areas at sufficient distance from the building.
- Test and maintain alarms.
- Post a person to meet/direct emergency vehicles.

Emergency Planning & Response



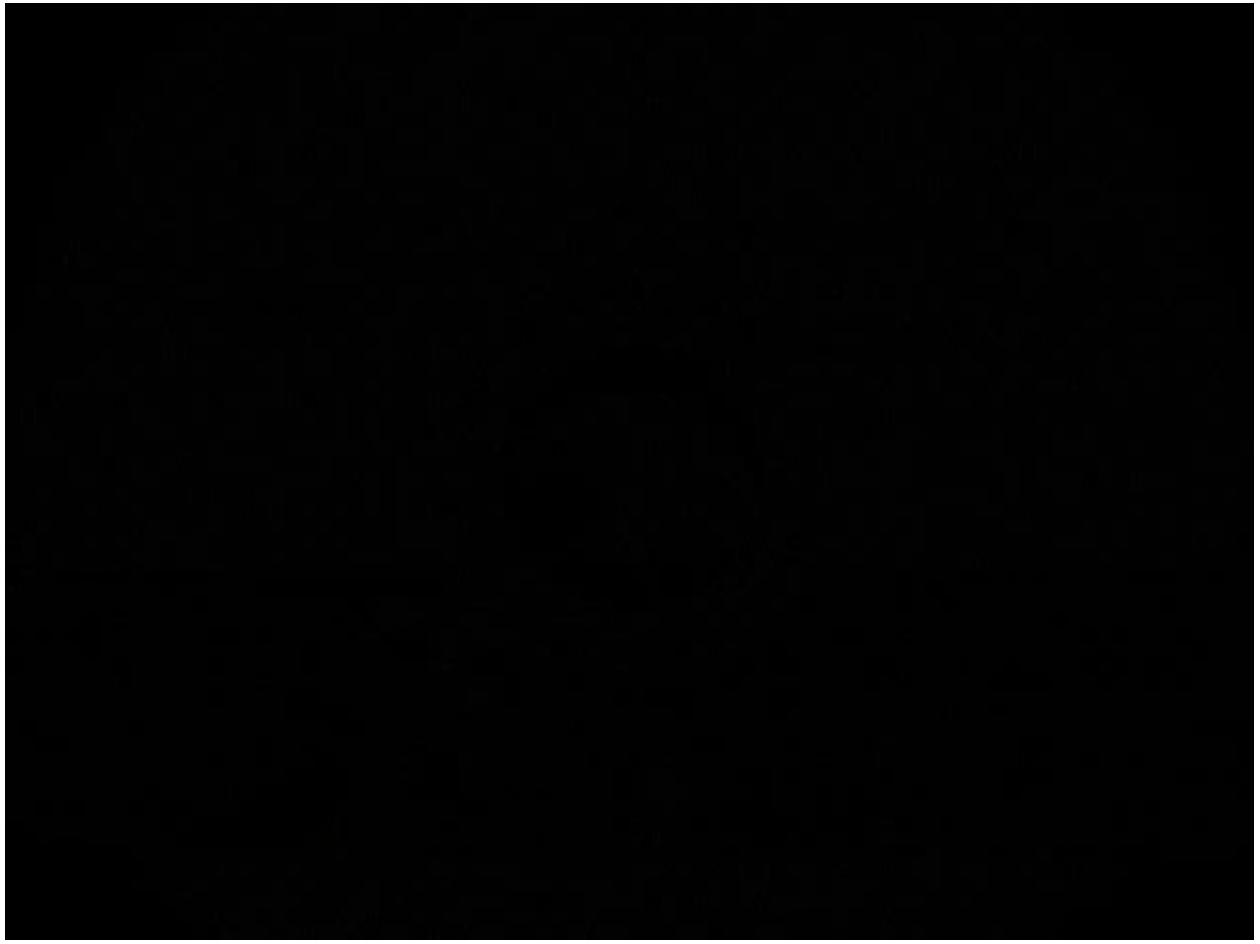
Alarm systems need to be properly located, maintained,

and serviced regularly

and

be suitable for all disabled workers.

Video – Explosion and Fire at T2 Lab



Emergency Planning and Response is based on principles of:

- Anticipation
- Recognition
- Evaluation
- Control

Preparing For Emergencies

- Emergencies
  - potentially life threatening
  - occur suddenly without warning
- Quick response will:
  - make difference between life and death
  - minimize damage
  - prevent panic, timely control
- Emergency responders
  - organize, stabilize, administer
- Adequate preparation requires
  - planning, practice, evaluation, adjustment

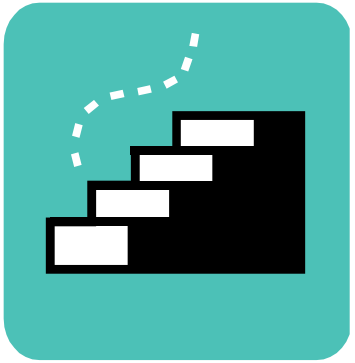
Emergency Management

- **Mitigate**
  - **eliminate / reduce occurrence or effects of an emergency**
- **Preparedness**
  - **plan how to respond; resources**
- **Response**
  - **assist victims, reduce damage**
- **Recovery**
  - **return to normal and assess**

Planning & Preparation

Anticipate types of emergencies:

- **Step-by-step procedures**
- **Assess resources available**
- **Coordinate with all responding agencies**
- **Chain of command**
- **Roles & assignments**
  - **Clearly spelled out and understood**
- **Accident prevention strategies**
- **First aid – inspect, date, replacements**
- **Site maps – update**
- **Train & practice**
- **Evaluate & improve**



Emergency Response Plan

Include all situations and conditions:

- **Weather emergencies:**
  - Flood
  - Tidal waves
  - Cyclones
  - Heavy rains
  - High winds
- **Fire**
- **Earthquakes**
- **Security breaches**
- **Distraught employees**
- **Medical Emergencies**
- **Student unrest**
- **Political unrest**
- **Explosion**
- **Evacuation**
- **Terrorism**

Prepare for and expect the unexpected

Emergency Action Plan

- **Have a written plan and distribute it to all employees, especially new employees:**
  - **Emergency escape/evacuation procedures & routes**
  - **Critical process emergency shutdown procedures**
  - **Procedures to account for evacuated employees**
  - **Rescue or medical duties if employees required to perform them**
  - **Procedure for reporting emergencies**
  - **Contact information for Q&A**
- **Alarm systems**
- **Training**

CSP
CHEMICAL SECURITY ENGAGEMENT PROGRAM

Emergency Response Plan

- Comprehensive employee training
  - General employee training
  - Specialized & emergency responders
  - Annual refresher training or drills
  - Untrained personnel should not participate
- Spill & emergency response plans
- Contingency plans
- Medical response/first aid
- Personal Protective Equipment
- Safety Data Sheet's
- Site maps
- Clean up procedures
- Decontamination techniques

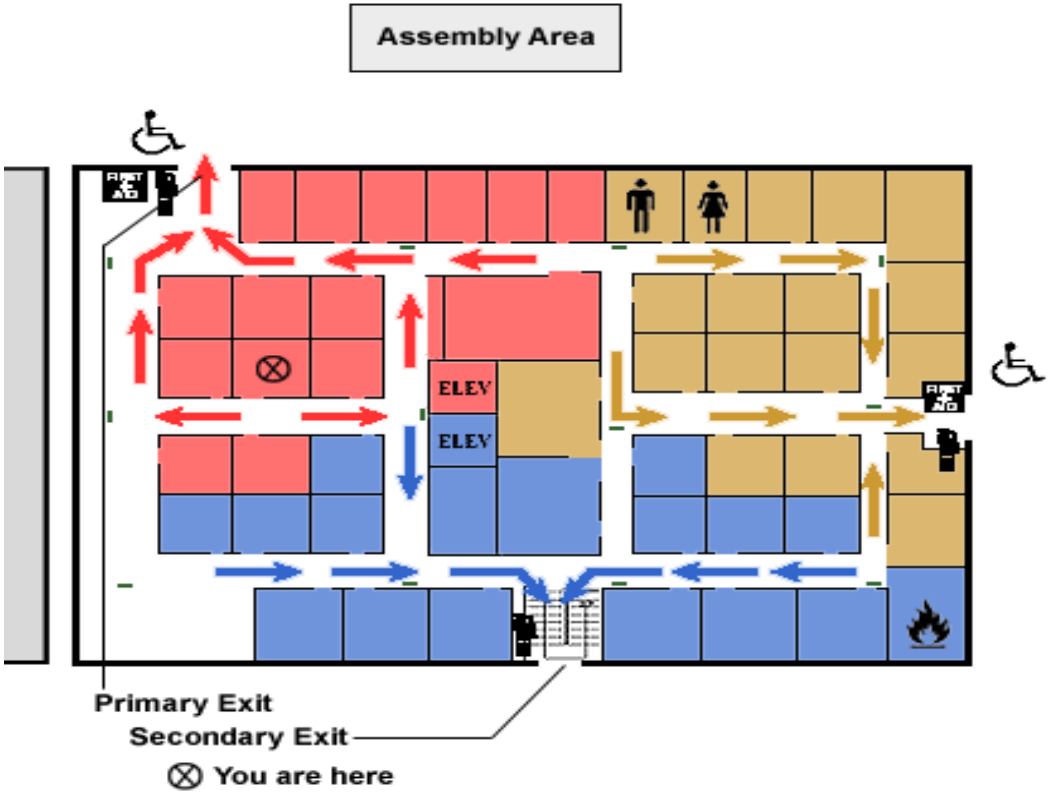
Include:
Fire Prevention Plan

- **Written plan**
  - List major fire hazards
  - Proper handling and storage procedures
  - Potential ignition sources & controls
  - Type of fire prevention systems
  - Contact information for those responsible for system maintenance
  - Contact information for Q&A
- **Housekeeping requirements**
- **Training**
- **Maintenance requirements**

Emergency Planning & Response

Have an evacuation plan for all buildings and areas and

POST IT



Emergency Planning & Response

Don’t use hallways for storage

Dangerous!!

Blocks passage and emergency exit path

Emergency Planning & Response

Label and keep all exits clearly.

Keep unlocked or equipped with panic bars.

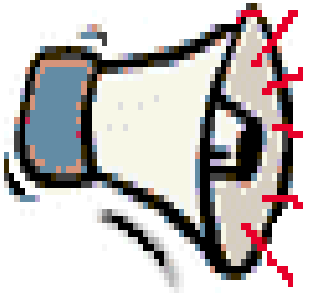
Emergency Planning & Response

- Have routine, unannounced evacuation drills.
- Test and maintain alarms.
- Designate person for each area to ensure bathrooms, etc. are evacuated.

- Locate outside staging areas sufficient distance from building.
- Designate person to meet/direct emergency vehicles.

Emergency Planning & Response

Alarm systems need to be properly located, maintained, and serviced regularly.



Alarm Systems: Reminder

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

Manual Pull Stations: Reminder

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

Remember:
People are reluctant to sound fire alarms!

Emergency Planning & Response

If people are expected to use extinguishers, they must be trained.

Emergency Planning & Response

Backup power

Does switch-over automatically?

How long will it run?

How much fuel do you have?

What areas will it support?

How often is it tested and maintained?

Emergency Planning & Response

Post each room with:

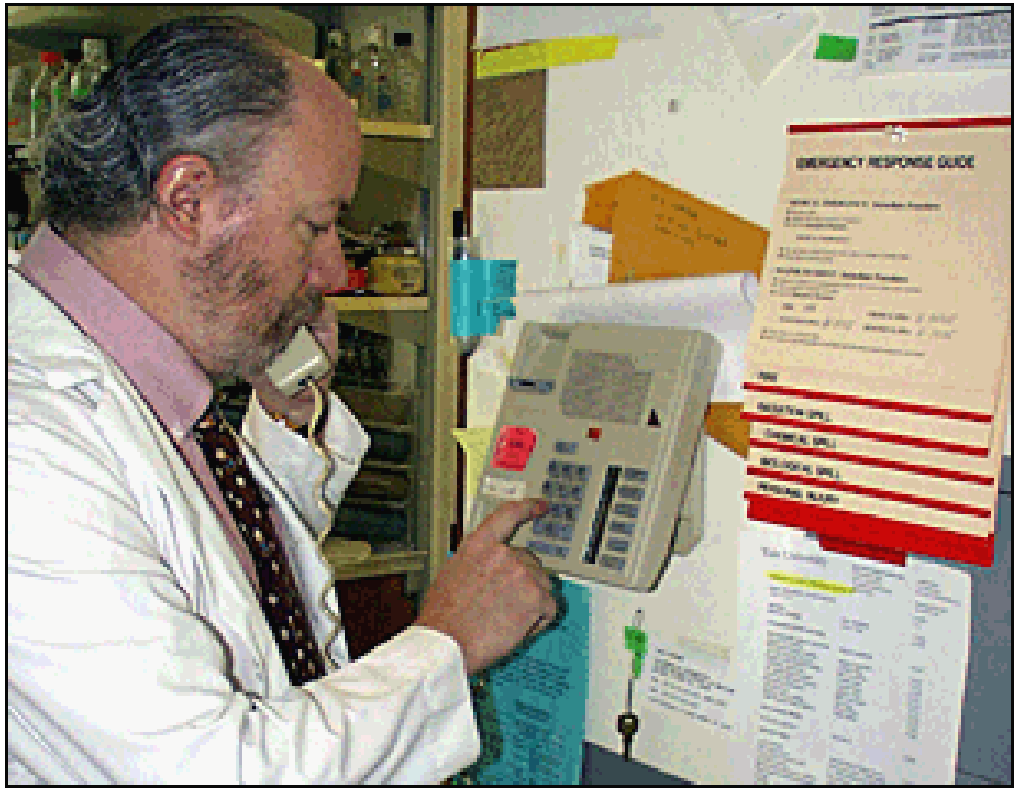
- **Emergency phone numbers**
- **After hours phone numbers**
- **Person(s) to be contacted**
- **Alternate person(s)**
- **Unique procedures to be followed**

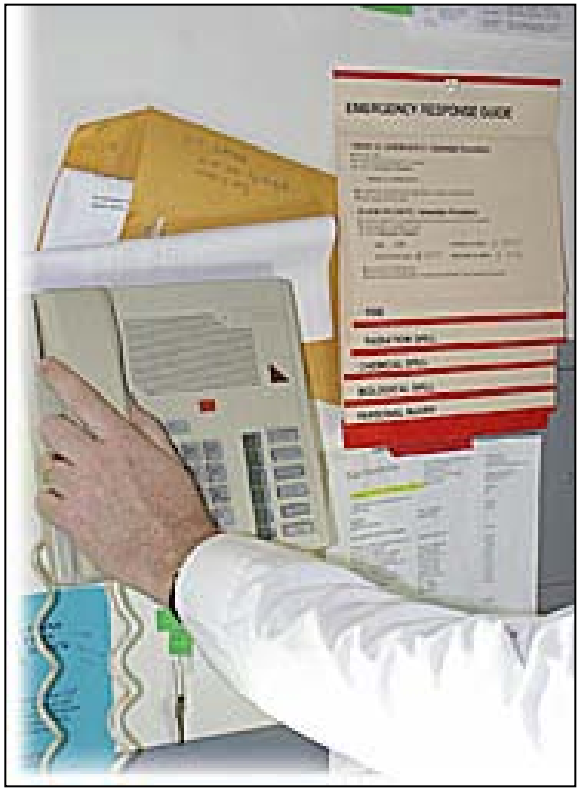
Location	
Hazards Within:	
Primary Contact:	
Second Contact:	
Building Monitor/Safety:	
Department Head:	
Fire/Police/Ambulance:	911
Envir. Health & Safety (or RSO, if needed):	646-3327

Emergency Phone Numbers

Clearly post emergency numbers

Do employees know what to do?





Emergency Planning & Response

Hoods should have low flow alarms.

Chemical specific toxicity alarms may be needed in certain areas.

Emergency Planning & Response

Centrally locate safety showers and eyewashes.

Schedule routine, periodic maintenance of all safety equipment.

Teach employees to properly use the Safety Shower

Time can make a difference…

Chemical Spills

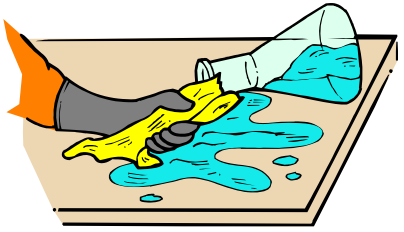
Centrally locate spill clean-up kits

Clean up spill only if you know the chemical hazards, have appropriate equipment and are trained to do so!

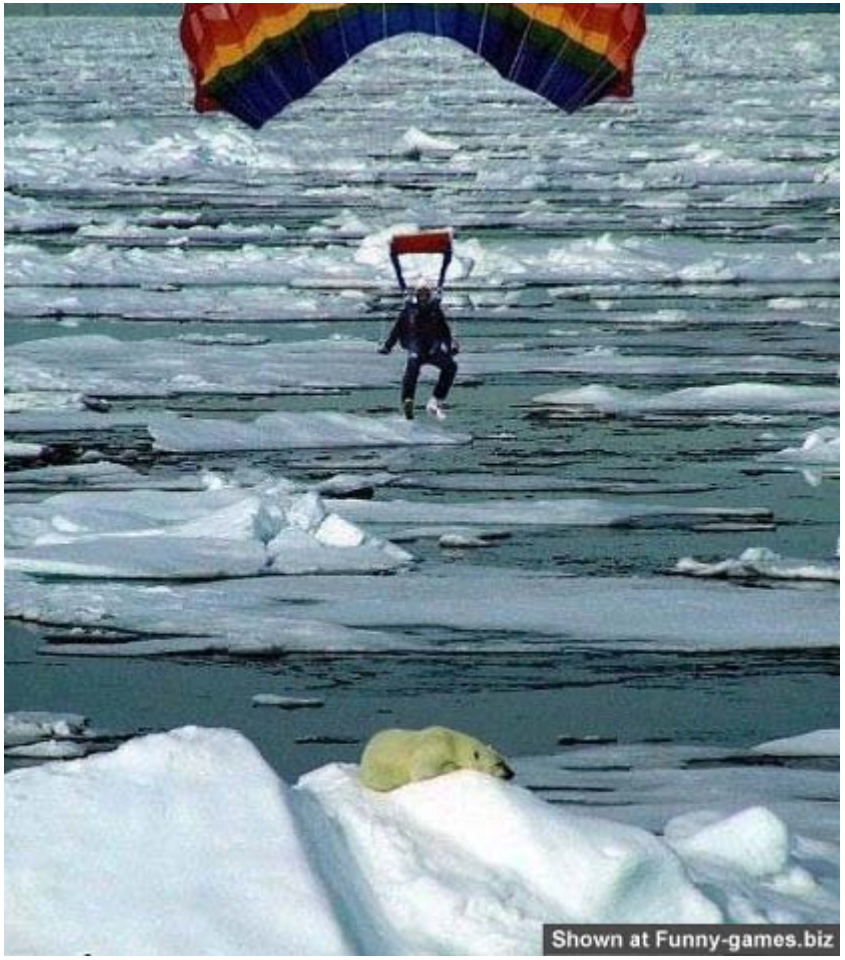
- Alert colleagues and secure area
- Assess ability to clean-up spill
- Find spill kit
- Use appropriate PPE and sorbent material
- Protect sinks and floor drains
- Clean-up spill, collect/label waste for disposal
- Report all spills

Centrally locate, inspect and maintain:

- First aid kits
- Special chemical antidotes, if necessary
- Respirators
- Specially train emergency personnel, if necessary
- Post inspection dates on equipment, including hoods



Always Expect the Unexpected



Principles and Concepts of Laboratory Design

Purpose of Laboratory Design

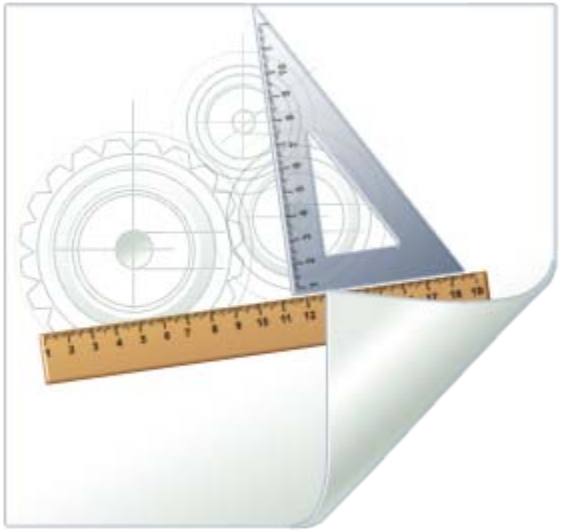
Protect the Workers

Enable the Work

Secure the Facility

Protect the Environment

Comply with Regulations



Objectives of Laboratory Design

- Provide a safe/secure workplace
- Facilitate workplace activities
- Efficient
- Cost Effective

Barriers to Good Lab Design

Cost

Poor Communication

Lack of Scientific Knowledge

Complicated Project

Trade-offs

Personalities

Maintenance

Good Laboratory Design

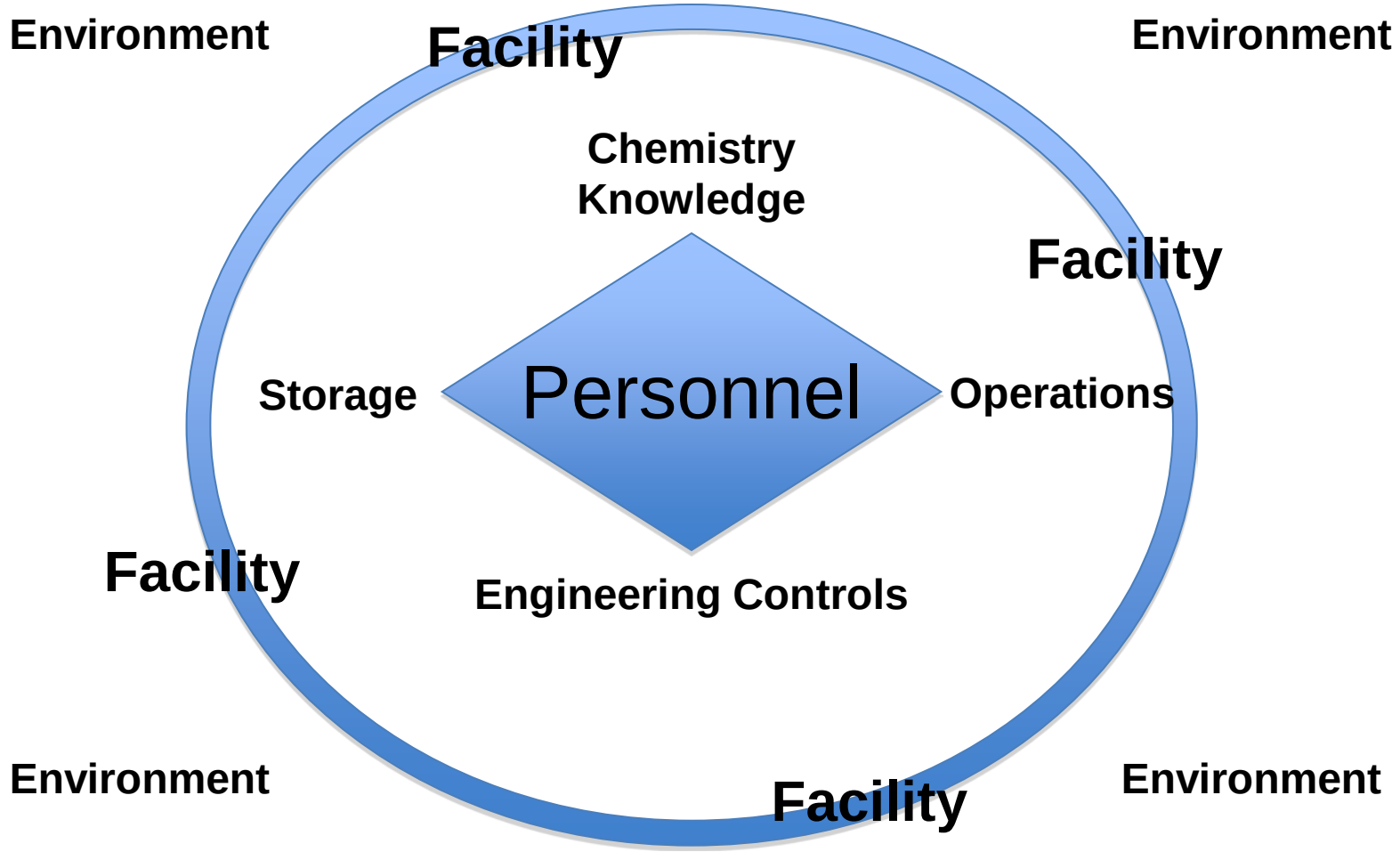
Based on:

Containment

Maximize Containment  **Minimize Contamination**

Redundancy is the Key

Chemical Containment Concept



Chemical Protection Depends on:

1
Chemistry Knowledge

Workers must have knowledge and understanding

2
Containment

Safe/Secure Storage

Proper Work Practices

Good Engineering Controls

Chemical Protection Depends on, cont'd:

3

Construction

How well the facility is built

Key Stakeholders

Architects

Engineers

Administrators

Builders

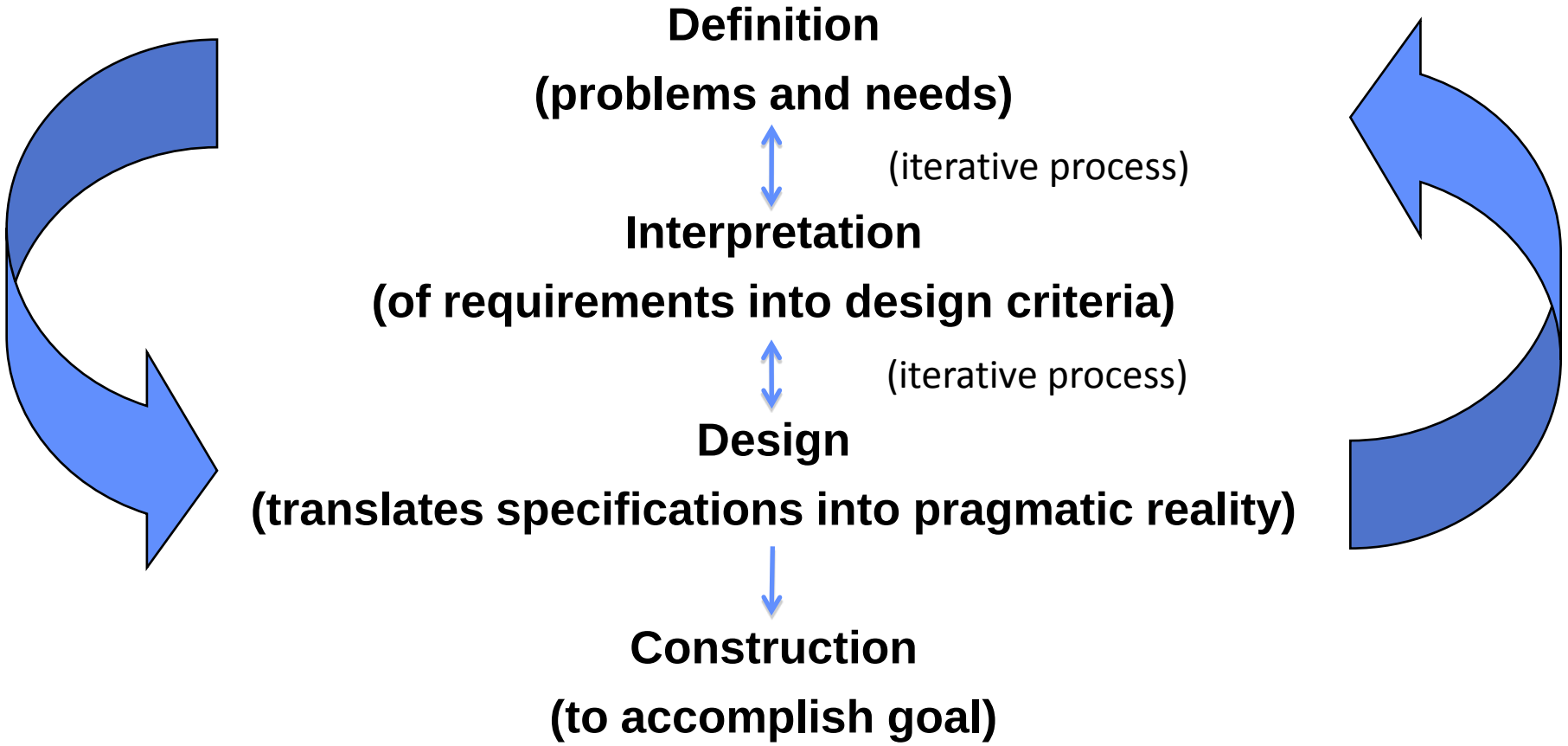
EHS Professionals

Laboratory Users

Laboratory Design

is an Iterative Process

Design Phases



Major US Standards & Guidelines

- **ANSI Z9.5: American National Standards Institute**
  - **Z 9.5 Laboratory Ventilation Standard**
- **NFPA: National Fire Protection Association**
- **BOCA: Building Officials Code Association**
- **ASHRAE: American Society of Heating, Refrigeration and Air Conditioning Engineers**
  - **Standard 110 for Testing and Evaluating Laboratory Hoods**
- **NIH Design Policy and Guidelines**
  - **National Institutes of Health**
    - **http://orf.od.nih.gov/PoliciesAndGuidelines/BiomedicalandAnimalResearchFacilitiesDesignPoliciesandGuidelines/policy-index.htm**
- **Others:**
  - **National Electrical Code**
  - **American Chemical Society – Green Chemistry Institute**
    - **www.acs.org/greenchemistry**

Architectural Features Include:

- Layout of buildings and laboratories
- Space requirements
- Spatial arrangement of equipment and benches
- Emergency egress
- Storage requirements
- Waste requirements
- Access controls
- Security features

Lab Design Components

- **Spatial**
  - Floor plan
  - Location of rooms and equipment
  - Traffic flow of people and equipment
  - Access control
- **Mechanical**
  - Ventilation
  - Utilities
  - Effluent control
  - Control and monitoring
- **Safety and Security**

Factors in Laboratory Design

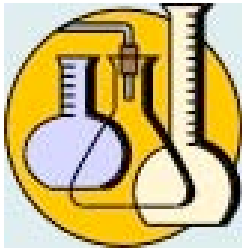
- **Architectural**
- **HVAC***
- **Safety and Security**
  - **Fire**
  - **Emergencies**
  - **Exposures**
  - **Access/exit control (facility, chemicals, equipment)**

(* heating, ventilation, and air conditioning)

General Information Needed

- Number of occupants and their technical qualifications
- Space and storage requirements
- Utilities needed
- Equipment needs
- Time/duration of occupancy
- Anticipated changes in research/programs
- Sustainability (environmental, green initiatives)
- Security needs

Safety/Security Information Needed Before Design can Begin



Type of Work/Research

Type of Hazards

Type of Wastes

Chemical

Biological

Radiation

High Voltage

Safety/Security Information Needed for Lab Design, cont'd.

Types of Chemicals
(based on physical state and properties)

Flammable

Corrosive (acid or base)

Reactive

Acutely Toxic (poisons)

Regulated

Chronically Toxic (e.g.,carcinogens, repro-toxins)

Chemicals of security concern

Controlled Drugs

Wastes

Specific Chemical Laboratory Safety/Security Concerns

Include:

- Fire detection, alarms, and suppression systems
- Safety equipment (i.e. emergency showers, eyewash and contaminant control)
- Ventilation (i.e. laboratory hoods, glove boxes, ventilated enclosures)
- Management of chemicals and waste
- Access controls for facility and laboratories

Examples of Lab Design Considerations

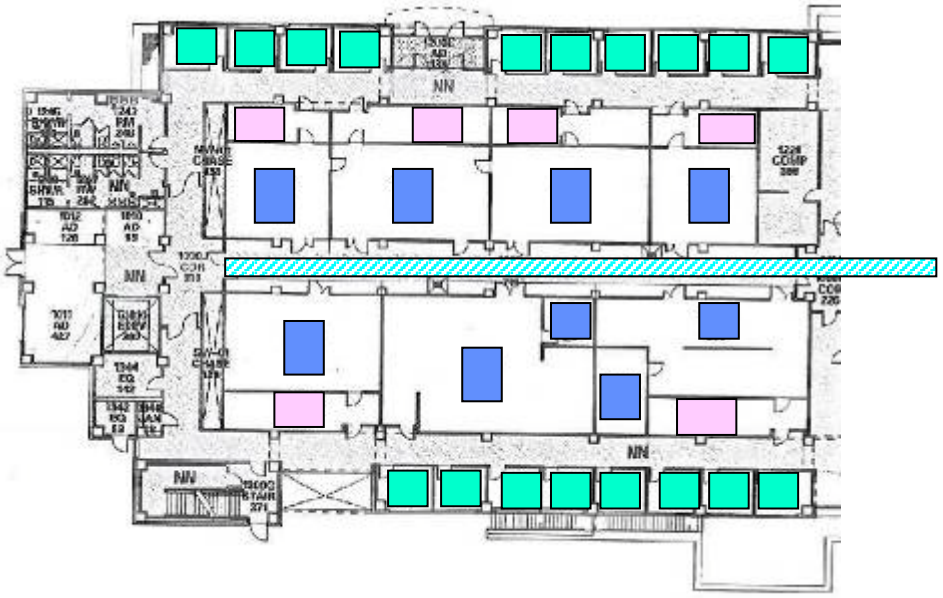
- Sample preparation and storage area
- Segregate sample digestion using acid-specialized laboratory hoods
- Segregate solvent extraction to reduce vapor contamination
- Proper eyewash placement
- Adequate egress
- Waste storage area
- Gas bottle storage

Building Layout: Divide into Zones

- Zones or control areas may have different:
  - Types and degree of hazards
  - Amounts of hazardous chemicals
- Allows better control over:
  - Personnel access
  - Hazards using
    - Equipment
    - PPE
    - Administrative procedures
- Examples: Fire safety zones, HVAC zones, Building floors

Building Layout: Corridors

- **Best practice is to separate movement of:**
  - **General population**
  - **Laboratory personnel**
  - **Chemicals and laboratory materials.**
- **Internal "service corridors" between labs**
  - **Allow transport of chemicals away from public**
  - **Provide access to utilities and other support equipment**
  - **Provide additional lab exits with emergency doors to main corridors**



General Lab	Staff Office	Chemical Free	Utility Corridor

Building Layout: Entrance/Exit Doors

- Good safety: two or more exits from each lab/room/building
- Good security: control who can enter a lab/room/building
- Emergency exit doors:
  - Lack handles or are locked on outside
  - Have “panic bar” on inside
  - May set off alarm when opened

Building Layout: Chemical Stockrooms

- Multiple, specialized stockrooms rather than one central storeroom
  - Chemicals dispensed across counter
  - Access restricted to stockroom personnel
  - Locked when unattended

- Teaching stockroom
  - High traffic
  - Only keep ~1 week supply of chemicals needed for student experiments
- Central Stockroom
  - Wide variety of chemicals and materials
  - Additional controls and containment for regulated, attractive, or dual-use chemicals
- Chemicals stored in compatible groups

Building Layout: Compressed Gases

- **Install tanks outside building and pipe into lab**
  - **Long-term, frequent use of same gas**
  - **Highly hazardous gases**
  - **Restrict access**
  - **Out-building or outdoors, depending on conditions**

Building Layout: Compressed Gases

- **Tanks inside labs**
  - **Wide variety of gases**
  - **Low use rates**
  - **Strap to wall or bench**
  - **Transport safely**

Building Layout: Chemical Waste

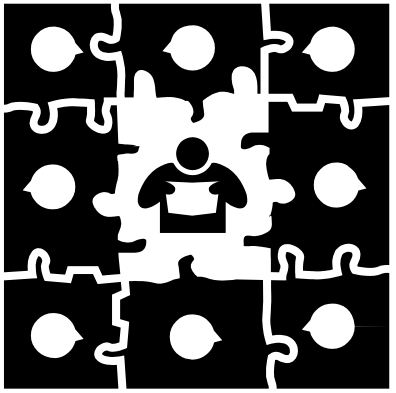
- **Large volumes of chemical waste should be stored in areas with fewer people**
  - **Access restricted to responsible personnel**
  - **Locked when unattended**
  - **Divided into chemically compatible groups**
  - **Provide safety equipment and alarms**

Building Layout: Chemical Waste

- **Waste collection area in teaching/research labs:**
  - **Convenient student use**
  - **Emptied/moved frequently**
  - **Divided into chemically compatible groups**
  - **Provide safety equipment**

Modular Laboratory Design

- Uses standard size and layout of benches, equipment and utility connections
- Customize layout for specific applications
- Allows for:
  - Cheaper lab design
  - Easier lab modifications
  - Easier lab renovations



Current Trends in Laboratory Design of Safety/Security Concern

- Open Laboratories
- Energy Conservation
- Ventilation Concerns
- Hood Designs
- Hood Manifold systems
- Effluent Modeling from Exhaust Stacks
- Lab Decommissioning

Open *vs.* Closed Laboratories

Open Laboratory

Closed Laboratory

Open *vs.* Closed Laboratories

Consider using both or having connected access:

Open laboratories

- Support team work
- Facilitates communication
- Shared:
  - Equipment
  - Bench space
  - Support staff
- Adaptable and flexible
- Easier to monitor
- Cheaper to design, build and operate
- The trend since mid 90's

Closed laboratories

- Specialized, dedicated work
- More expensive
- Less flexible
- Easier to control access
- Needed for specific work
  - NMR
  - Mass spec
  - High hazard materials
  - Dark rooms
  - Lasers

Energy Conservation, Sustainability and Green Chemistry Concerns

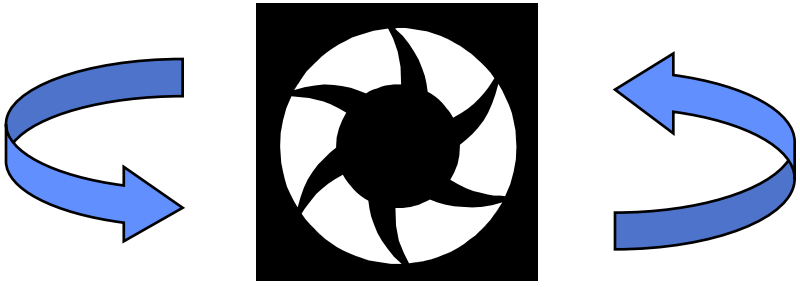
- Design leading to increased productivity
- Energy conservation and efficiency
- Centralized heat-generating equipment
- Manifolded hoods and ventilation
- Reduction/elimination of harmful substances and waste
- Efficient use of materials and resources
- Recycling and reuse

Energy Conservation Issues

- Vented Enclosures
- Ductless Hoods
- Diversity
- Manifolded Systems
- Recirculation of Room Exhaust Air
- Variable Air Volume Systems
- Automatic Sash Closers
- Air Change per Hour
- Low Flow Hoods

Ventilation Considerations Include

- Heating and cooling needs
- Maintaining directional airflow
- Type of hoods
- Single vs. manifolded hoods



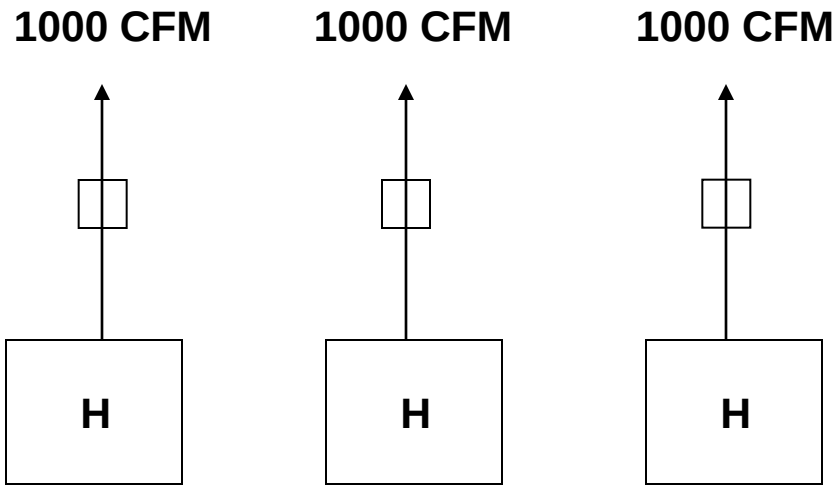
Laboratory hood design and ventilation are discussed in detail in later presentations.

General Laboratory Hood Considerations

- Determine minimum exhaust requirements.
- Communicate hood limitations to users.
- Label restrictions e.g., no perchloric acid.
- Alarm systems
- Consider future needs.

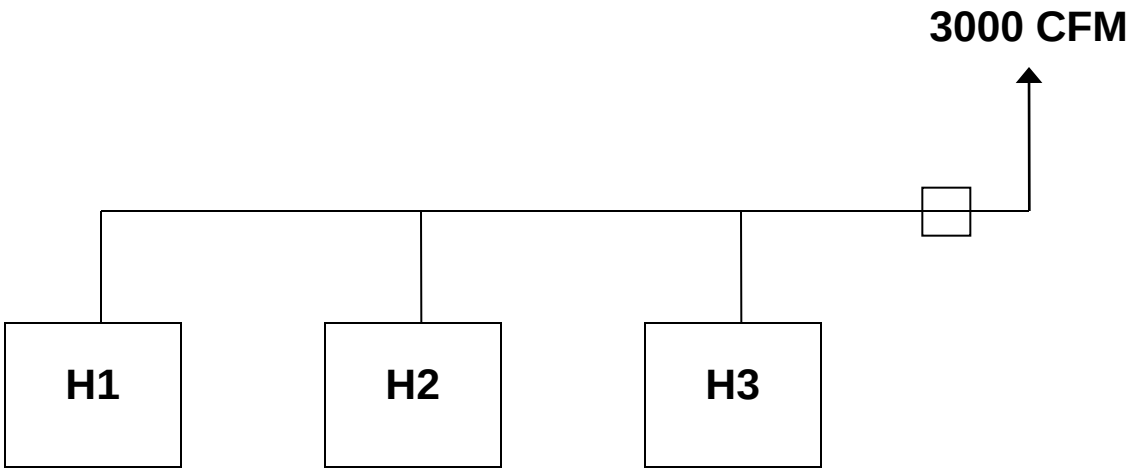
Hood Manifold Considerations

Single Hood - Single Fan



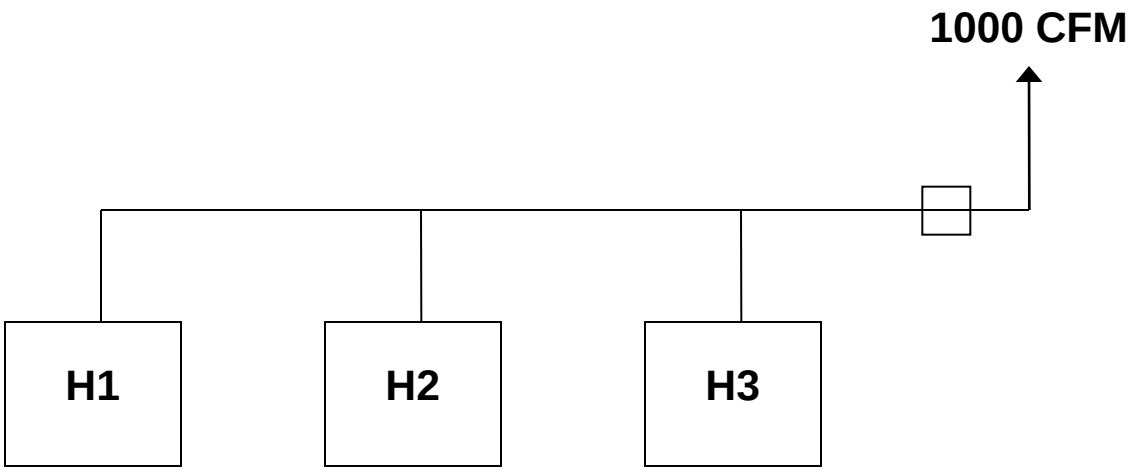
Hood Manifold Considerations

Manifold: 3 Hoods, 1 Fan

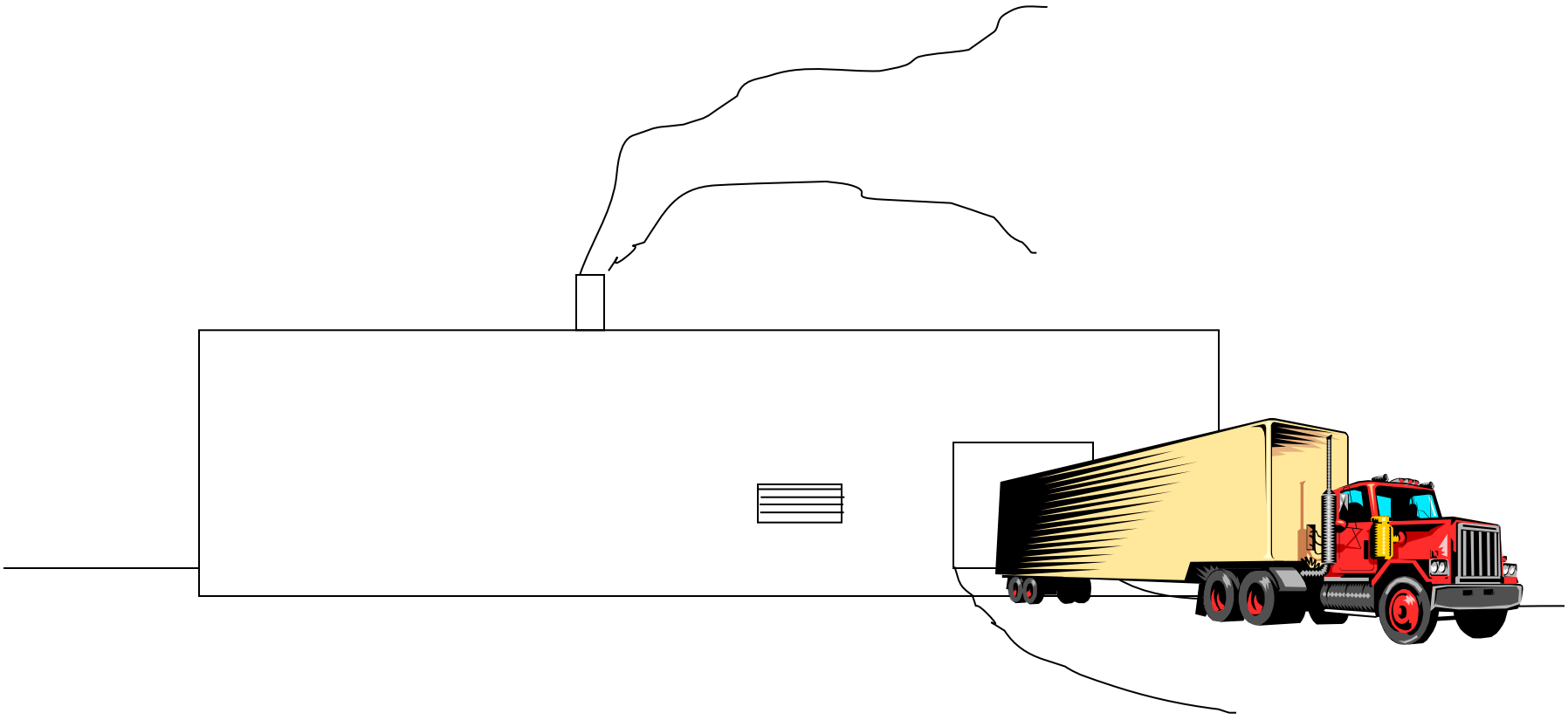


Hood Manifold Considerations

Hood Diversity = 33%



Ventilation Design: Avoid Exhaust Recirculation



350

Lab Layout

- Try to locate hoods, utilities and safety equipment in the same relative position in all labs.
- Locate sinks centrally
- Space between benches should allow people to pass each other (≥1.5 m).
- Details given in later presentations on:
  - Lab hoods
  - Safety showers / eyewashes
  - Chemical management

Lab Layout

- Construction materials should be appropriate for chemicals
  - Benchtops
  - Cabinets & shelving
  - Flooring
  - Avoid metal drainpipes
- Store chemicals and waste securely – not easily spilled or knocked over.
- Keep bulk chemicals in stockroom - not lab.
- Control access to labs, especially during off-hours

Laboratory Modifications or Decommissioning

- When a laboratory is modified or vacated, ensure that:
  - Chemicals have been safely moved to another lab, returned to the stockroom, or properly disposed of.
  - Any contamination has been removed from the:
    - Room (floor, ceiling, walls)
    - Furniture
    - Equipment and fixtures
    - Plumbing system
    - HVAC ductwork

Conclusion

Together we can design, build,
and operate safe/secure laboratories!