Chemical
SAFETY AND SECURITY TRAINING

Workshop

Indonesia
August 2009

SAND No. 2008-3832C
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 Dual-use Awareness

Pauline Ho, PhD

International Chemical Threat Reduction Department
Sandia National Laboratories

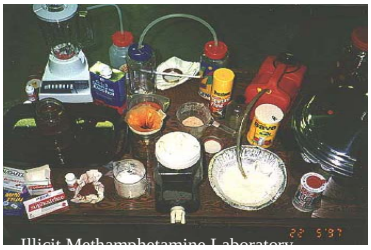
Chemical SAFETY AND SECURITY TRAINING

Chemical dual-use awareness

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

Dual-use chemical example: Pseudoephedrine

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



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

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

Dual-use chemical example: Cyanide

Therence Koh/AFP/Getty Images

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

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

Dual-use chemical example: Pesticides

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

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

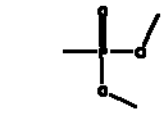
Photo/New York City Poison Control Center

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

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

Many lab/industrial chemicals have dual uses

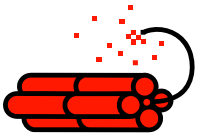
- **Dimethyl methyl phosphonate (DMMP)**
  - **Flame retardant for:**
    - **building materials, furnishings, transportation equipment, electrical industry, upholstery**
  - **Nerve agent precursor**
- **Thiodiglycol**
  - **Dye carrier, ink solvent, lubricant, cosmetics, anti-arthritic drugs, plastics, stabilizers, antioxidants, photographic, copying, antistatic agent, epoxides, coatings, metal plating**
  - **Mustard gas precursor**
- **Arsenic Trichloride**
  - **Catalyst in CFC manufacture, semiconductor precursor, intermediate for pharmaceuticals, insecticides**
  - **Lewisite precursor**



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

Dual-use Chemicals: Explosives

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



Theft / manufacture of explosives: Fertilizer Bomb

Photo: US DOD

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

Diversion of industrial / laboratory chemicals: Sodium azide

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

Diversion of industrial / laboratory chemicals: 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

Chemical Management Best Practices

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

Environmental & Chemical Safety Educational Institute

Chemical Management

Best Practices

References

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

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

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

Chemical Management

Institute a Safety Program

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

Cradle - to - grave care of chemicals

Receipt → **Storage** →

Use → **Disposal**

Plan experiments in advance!

What chemicals are needed?

How much is needed?

How will the chemicals be handled?

What are the reaction products?

How will the chemical be stored?

How will disposal take place?

Inventory management

Less is Better !

- Order only what you need
- Reduce size of experiment
  - It 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

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

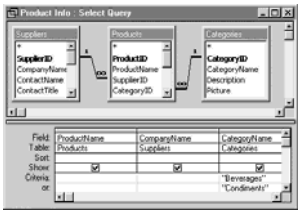
Inventory and tracking

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 MSDS
- Chemical Inventory Search Menu
- Chemical Regulatory Reports Search Menu
- Find Chemical Storage Locations

Transfers, Removal, Verification and Inventory Entry:
- Transfer or Remove a Barcode from the Chemical 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

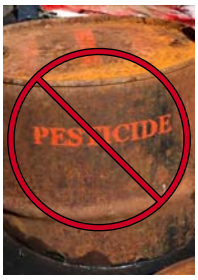
Requester search

Barcode search

Inventory management

- How old are your chemicals?

- Some chemicals degrade over time
  - rotate stock
  - label & date



Inventory management

Less is Better !

It's Safer!

It may be cheaper to order **diethyl ether** in large containers

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

Inventory management

-R-O-O-R-

Peroxide Forming Chemicals

Even with inhibitors they can become dangerous over time

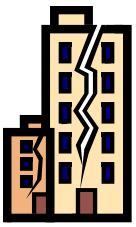
Examples: ethers, dioxane, tetrahydrofuran

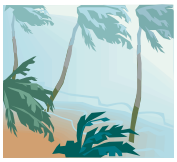
- **discard or test if unsure**
- **label & date when received, when opened, and provide expiration date**

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

Chemical storage

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





Chemical storage: Basic concepts

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

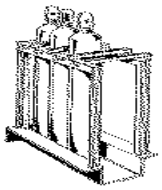
Use flammables storage cabinets

Chemical storage: Basic concepts

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

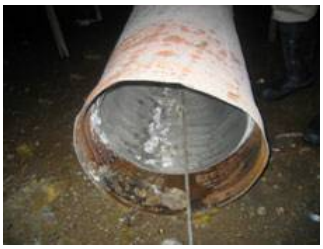
Chemical storage: Gas cylinders

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



Improper gas cylinder storage

Gas Cylinders



Exploded nitrogen cylinder

Chemical storage: Cryogenics

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

Chemical storage: Good practices

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

Chemical storage: Bad practices

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

Chemical storage: Containers

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

Improper chemical storage

Never use hallways for storage

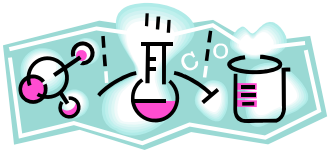
Safety Hazard!!

Blocks exit path in emergencies!!!

Suggested shelf storage groups: Organics

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

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

Chemical Management: Recycling

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

Environmental & Chemical Safety Educational Institute

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 <u>not</u> 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?

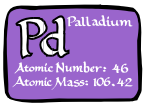
- Excess unopened chemicals
- Excess laboratory glassware (unused or clean)
- Consumables with no expiration
- Solvent that can be purified
  - Lower purity suitable for secondary use?
- Precious or toxic metals
  - Hg, Ag, Pt, Pd, Au, Os, Ir, Rh, Ru
- Others?

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

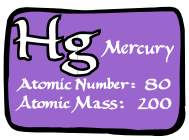
Recovery from chemical oxygen demand (COD) test
- Acidification and ppt as AgCl

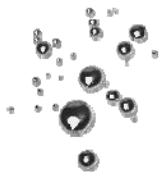
Recovery from photographic fixing solution
- Precipitate as sulfide
- Precipitate with TMT (trimercapto-s-triazine)
- Electrolysis (terminal and in-line)
- Metal replacement (iron containing cartridges)
- Ion exchange

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





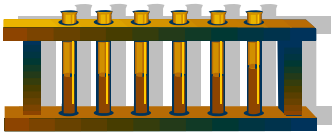
Solvents can be recovered by distillation

- 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

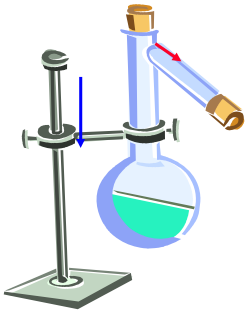
Solvent recycling – low efficiency

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

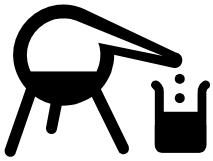
Distillate

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

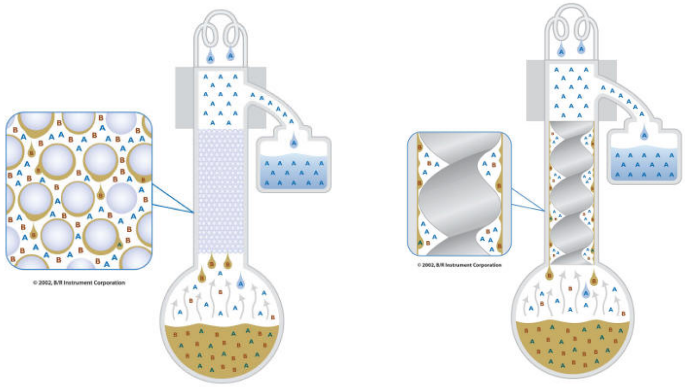


Example: 200mm long column for separating benzene and toluene

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}

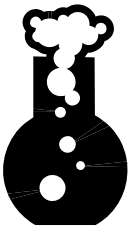
Boiling point of common solvents (C)

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

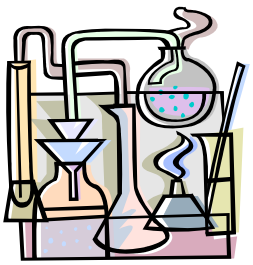
Individual Substances
- **Di-isopropyl ether (isopropyl alcohol)**
- **Nitromethane**
- **Tetrahydrofuran**
- **Vinylidene chloride (1,1 dichloroethylene)**



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**



Need to clarify wording of these examples.

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/

Chemical Management: Waste

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

Environmental & Chemical Safety Educational Institute

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)**

Substitute reagents to reduce waste

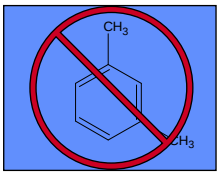
•Citrus based solvents for xylene in histology lab

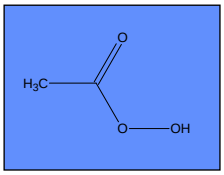
•Peracetic acid for formaldehyde for cleaning kidney dialysis machines

•Non mercury thermometers

•Enzyme and peroxide based cleaners for chromerge (NoChromix)

•When purchasing automated equipment think of chemical waste





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

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

PCDD = polychlorinated dibenzodioxin
PCDF = polychlorinated dibenzofurans
PAH = polycyclic aromatic hydrocarbon
VOC = volatile organic compound

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

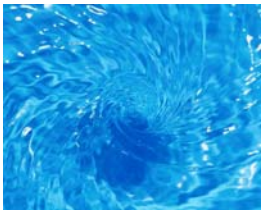
Waste management: Waste disposal service

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

Waste management: Down the drain?

If legally allowed:

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



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

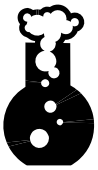
- **Activated carbon**
- **Ion exchange resin**
- **Activated alumina**

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)

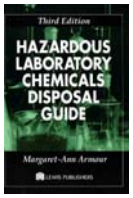
- Active halogen compounds with NaOH
- Carboxamides with HCl

Oxidation-reduction

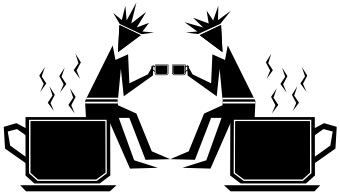
Handbook of Laboratory Waste Disposal, Martin Pitt and Eva Pitt, 1986. ISBN 0-85312-634-8

Waste management: Treatment in Lab?

- Destruction / neutralization of hazardous chemicals
  - May or may not be allowed by regulations
  - Must be done by trained chemist
  - Specific to each chemical
- References:
  - "Procedures for the Laboratory-Scale Treatment of Surplus and Waste Chemicals, Section 7.D in Prudent Practices in the Laboratory: Handling and Disposal of Chemicals," National Academy Press, 1995, available online: http://www.nap.edu/catalog.php?record_id=4911
  - Handbook of Laboratory Waste Disposal, Martin Pitt and Eva Pitt, 1986. ISBN 0-85312-634-8
  - "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



Break



Breakout Discussion: Chemical Management and Next steps

- Break into smaller groups
- Discuss what you think should happen next
  - 45 minutes
- Report back action items to group

Emergency Planning and Safe/Secure Transport of Chemicals

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

Environmental & Chemical Safety Educational Institute

Emergency planning and response is based on safety principles of

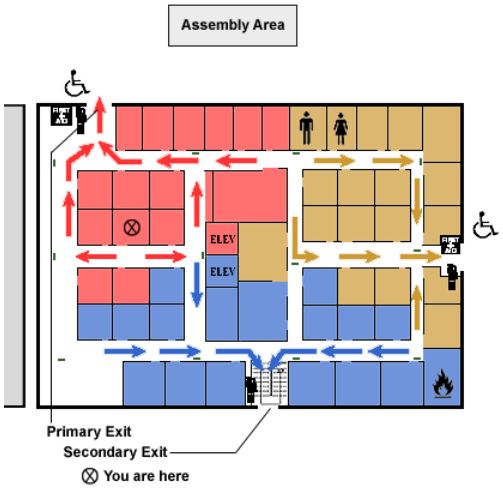
- Anticipation
- Recognition
- Evaluation
- Control

Emergency Planning & Response

Have an evacuation plan

and

POST IT



Emergency Planning & Response

Don't use hallways for storage

Dangerous!!

Blocks passage and emergency exit path

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

Emergency Planning & Response

Centrally locate and maintain fire extinguishers and alarms

Emergency Planning & Response

If people are expected to use extinguishers

they must be trained

Emergency Planning & Response

Post each room with:

- **Emergency phone numbers**
- **After hour 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):	846-3327

Emergency Planning & Response

Label and keep all exits clear, unlocked or equipped with panic bars

Chemical Exposures to Eyes or Skin

Centrally locate safety showers and eyewashes

- Remove contaminated clothing
- Thoroughly flush with water
- Follow chemical specific procedures (i.e.. HF)
- Seek medical assistance

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

International transport references

UNECE, "Globally Harmonized System Of Classification and Labeling of Chemicals (GHS)," 1st edition, 2003, online,

http://www.unece.org/trans/danger/publi/ghs/ghs_rev00/00files_e.html

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

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

UN International Maritime Organization (IMO),

http://www.imo.org/

European Union (EU) Transport Activities

http://europa.eu/

US Department of Transportation (DOT)

http://www.dot.gov

International Shipping Fines

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

What is a hazardous chemical shipment?

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

Forms of transport

Outside of facility:

- air
- ship
- rail
- road

Within a facility:

- vehicle (car / truck)
- cart
- hand carry

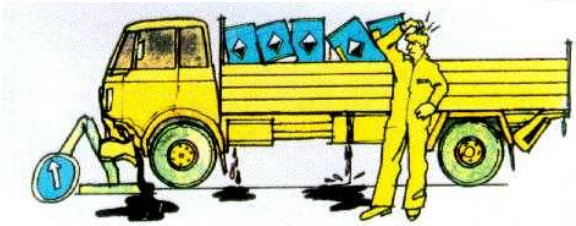
Always know

- Who transports the material?
- How is it transported?
- How is it packaged?
- Are transporters knowledgeable and prepared?
- Is there safety documentation?
- When did it leave, arrival time?
- Verify departure and arrival

Always expect the unexpected

Take Precautions

- Proper Packaging
- Spill and leakage protection

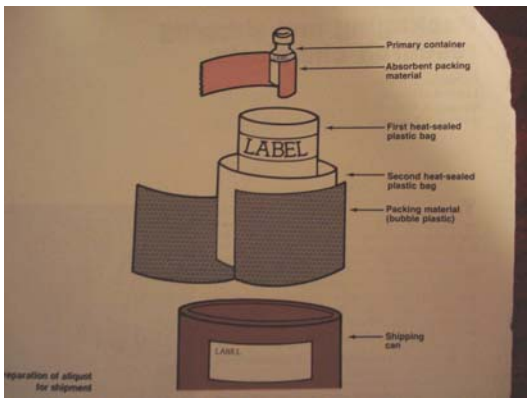


Small spills from many cars daily: when counted together make...

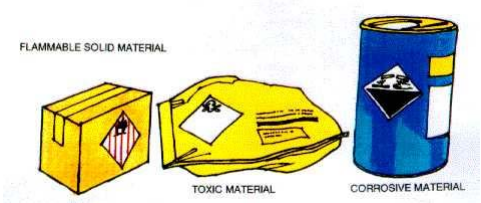
Special shipping requirements?

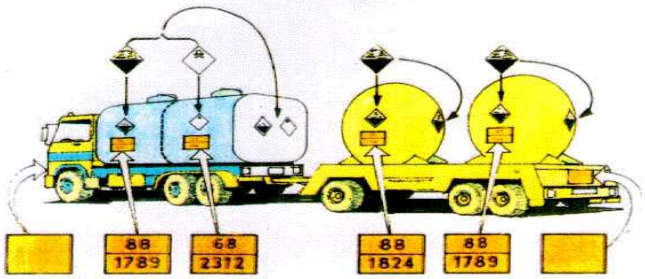
- What are the physical and chemical properties?
- Is dry ice or refrigeration necessary?
- Are specific containers required? size, strength, composition

Container within a container concept



Labels and Placards





Labels continued

- Properly and fully identify material
- Use:
  - proper, full chemical name
  - no abbreviations
  - use ID codes, e.g., UN Numbers
- Specify
  - quantities
  - concentrations
  - number of containers
- Indicate specific hazard class
- Include:
  - Emergency Information
  - Contact names
  - 24/7 phone numbers
- Use appropriate language(s) and *universal* symbols

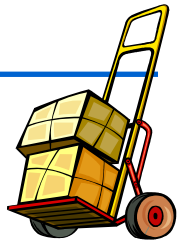
Documentation

- Shipping Order
- Bill of lading
- Manifest
- Full addresses for Shipper and Receiver
- Packing and Labeling Certification
- Verification of Receipt
- *Safety Data Sheets*
- Follow-up documentation
- Require incident/accident reports


FLINN SCIENTIFIC INC.
"Your Safer Source for Science Supplies"
Material Safety Data Sheet (MSDS)
Acetic Acid: Glacial

Handling

- Where, how, who – packs the shipment?
- Is there special equipment needed to load and unload a shipment?
- Where, how, who – opens the shipment?
- Should package be opened in a hood?
- Is the material radioactive?
- Is monitoring equipment needed?
- Is special storage needed on receipt?



Who requires training?

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

Emergency Preparation

- **Transportation accidents/incidents:**
  - **Organization reports**
  - **Police reports**
  - **Emergency contacts**

- **Spill and leakage control:**
  - **prevention**
  - **minimization**
  - **spill clean up kits**
  - **PPE**

Who is responsible of damages if a leaking drum spills dangerous material? You?

Plan ahead

- **Have a plan**

- **Remember:**
  - **Anticipation**
  - **Recognition**
  - **Evaluation**
  - **Control**

Safety equipment should have a routine check.

Acknowledgment

International Labour Organization (ILO)

International Occupational Safety and Health Centre (CIS)

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

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

Components of Chemical Security and Relationships Between Chemical Safety and Security

Pauline Ho, PhD

International Chemical Threat Reduction Department
Sandia National Laboratories

Chemical Security

- Is your Department secure?
- How easy would it be for someone to steal chemicals?
- Are your chemistry stockrooms, classrooms and research 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

Chemical Security: Personnel Management

- Guard against both Insider and Outsider threat
- Does anyone check on 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

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 ordering chemicals in the name of your institution but diverting them?

Chemical Security: Assign Responsibilities

- Identify people who will be responsible for various chemical security activities
  - Physical security and building modifications
  - Chemical tracking and reporting
  - Personnel and access management
  - Information management
  - Emergency planning
- Ensure that they have the time and resources to do the job
- Integrate with chemical safety responsibilities

Chemical Security: Professional behavior

- A Chemical Professional needs to use their scientific knowledge in a responsible manner

- A Chemical Educator needs to train their students to use their scientific knowledge in a responsible manner

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 on hand
- 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.
  - Alert community and especially emergency responders to possible chemical dangers.
  - 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, we want people to be able to leave the facility quickly and by many routes.
  - For security, we want to control exits as well as entrances so chemicals (or equipment) don't get 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 policies 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

Summary

- **Chemical safety and security are important**
  - **Academic chemistry laboratories are an attractive target for theft of chemicals**
- **Chemical safety and security measures have a lot of overlap**
  - **Attitudes and awareness**
  - **Policies**
  - **Physical additions/changes to buildings and labs**

Workshop evaluation and feedback form

- **Please help us improve this workshop by filling out and returning this form.**