



## Chemical Safety and Security Officer Training

**Irbid, Jordan**  
**February 2010**



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Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company,  
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under contract DE-AC04-94AL85000.





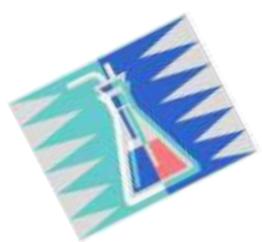
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# Lab Visit



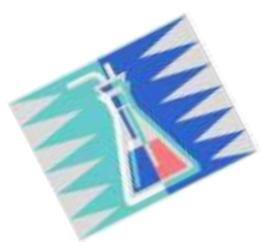
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**BREAK**



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# Chemical Safety Calculations



# Chemical Exposure

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How many g of ethyl alcohol must be evaporated into a room that is 7 m × 11 m × 3 m to reach the TLV of 1000 ppm? (MW 46)

Room Volume = 7m × 11 m × 3 m = 231 m<sup>3</sup>

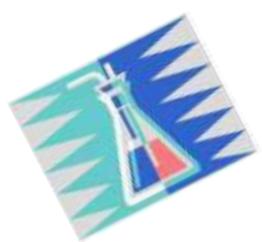
1000 ppm of EtOH corresponds to:

$$1\text{E-}3 \times 46.1 \text{ g/mole} / 24.45\text{E-}3 \text{ m}^3/\text{mole} = 1.885 \text{ g/m}^3$$

Multiply this concentration by the room volume

$$1.885 \text{ g/m}^3 \times 231 \text{ m}^3 = 435 \text{ g}$$





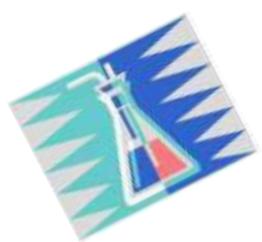
# Chemical Exposure

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A drop of contaminant is added to a bucket of water. Approximately how many ppm does this represent? (Assume 20 drops per ml and a 20 liter bucket.)

One drop is  $1/20 = 0.05$  ml

$5E-5$  liters/20 liters =  $2.5 E-6 =$  **2.5 ppm**



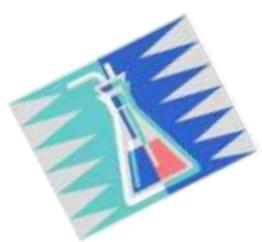
# Calculating TLVs for Mixtures

For mixtures of liquids where the compounds have similar toxicological properties, it is an accepted practice to calculate a TLV for the liquid mixture as a whole. The assumption is that the toxicological properties are additive in nature. A common application is to a mixture of solvents used in a dip tank or cleaning process.

$$TLV_{mixture} = \frac{1}{\frac{F_1}{TLV_1} + \frac{F_2}{TLV_2} + \frac{F_3}{TLV_3} + \dots + \frac{F_n}{TLV_n}}$$

Where  $F_n$  is the weight fraction of the  $n$ th component, and  $TLV_n$  is the corresponding TLV.

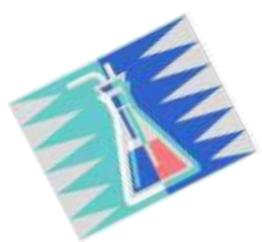




# Calculating TLVs for Mixtures

What is the TLV in  $\text{mg}/\text{m}^3$  for a solution containing 25% Naptha (rubber solvent, TLV  $1370 \text{ mg}/\text{m}^3$ ), 15% toluene (TLV  $377 \text{ mg}/\text{m}^3$ ) and the remainder Stoddard solvent (TLV  $525 \text{ mg}/\text{m}^3$ ).

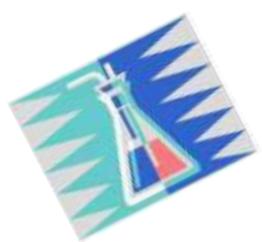
$$\begin{aligned} TLV_{mixture} &= \frac{1}{\frac{0.25}{1370} + \frac{0.15}{377} + \frac{0.60}{525}} = \frac{1}{1.824E-4 + 3.978E-4 + 1.1124E-3} \\ &= \frac{1}{0.001723} = 580.4 \text{ mg}/\text{m}^3 \end{aligned}$$



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## Lab Safety Activity:

**What's Wrong With These Pictures?**



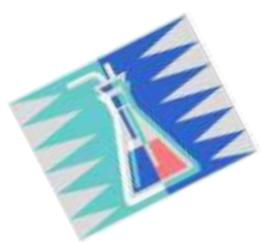
# What's Wrong With This Picture?





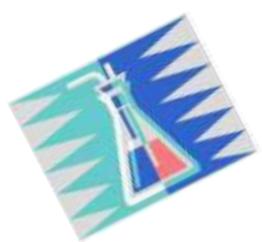
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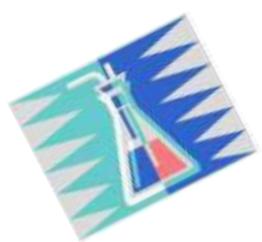
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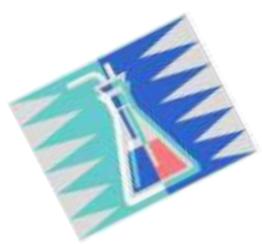
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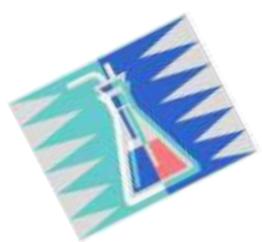
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# LUNCH



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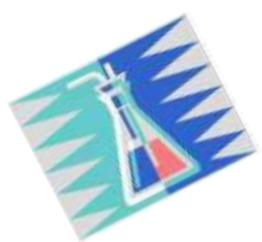
# Pesticide Management



# History of Pesticides

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

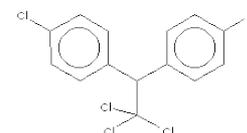




# Main pesticide categories

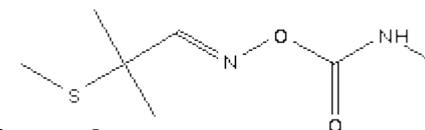
- **Organochlorines:**

- **Chlordane, DDT, Dieldrin, 2,4,5-T, Lindane, Heptachlor, Pentachlorophenol, Endrin, Aldrin, Chlordecone, Endosulfan, Hexachlorobenzene, Methoxychlor, Mirex, Toxaphene, TDE.**
- Chemical warfare agents: sulfur mustard, HD.



- **Organophosphates:**

- Esters of phosphoric acid, Parathion, Malathion, Methyl Parathion, Chlorpyrifos, Diazanone, Dichlorvos, Phosmet, Tetrachlorvinphos, Azinphos Methyl, Naled, Fenthion, Dimethoate, Acephate, phosalone and others.
- Chemical warfare agents: sarin, tabun, soman and VX.



- **Carbamates:**

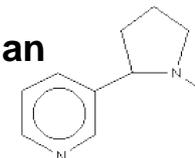
- Carbaryl, Sevin, Aldicarb, Carbofuran, Furadan, Fenothiocarb

- **Pyrethroids:**

- Synthetic chemical compound similar to natural pyrethins produced by the flowers of pyrethums (*Chrysanthemum cinerariaefolium* and *C. coccineum*).
- Common in household insecticides and insect repellent. At concentrations used in such products, they are generally harmless to human beings, except sensitive individuals.

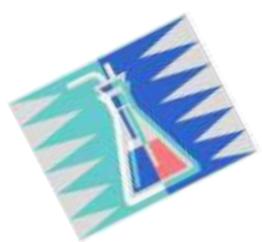
- **Neo-nicotinoids:**

- Synthetic analogs of nicotine insecticides, exhibit much lower mammalian toxicity and greater field persistence.
- Used in place of organophosphates and carbamates



**Red: banned by Stockholm Convention**

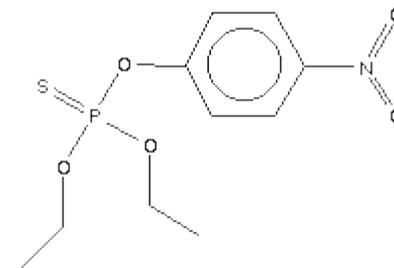




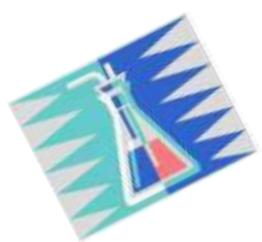
# Pesticides categorized by toxicity

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

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



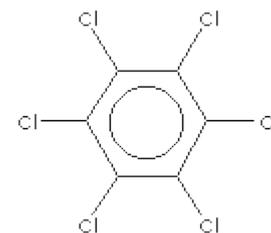
“The WHO Recommended Classification of Pesticides by Hazard and Guidelines to Classification, 2004”, updated June 2006, [http://www.who.int/ipcs/publications/pesticides\\_hazard\\_rev\\_3.pdf](http://www.who.int/ipcs/publications/pesticides_hazard_rev_3.pdf)



# Bad effects/properties of pesticides

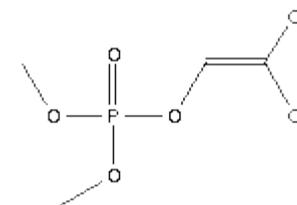
- **Organochlorines**

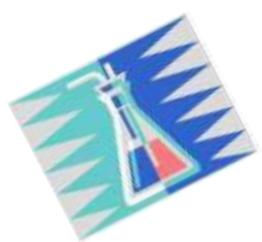
- Accumulates in human adipose tissue and human breast milk
- Accumulates and persists in animal milk and dairy products
- Interferes with estrogen and androgen receptors
- Suppresses immune system
- Targets sodium ion channels making powerful convulsants
- Can induce neurobehavioral problems
- Can cause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



- **Organophosphates,**

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





# Problems with pesticide use

- **Persistence**

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



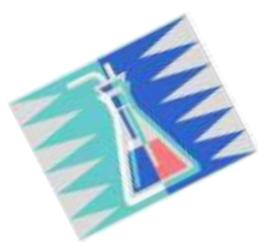
- **Non-discrimination**

- Improper use or application leads to the elimination of all arthropod species and severe consequences for other wildlife.
- Can contribute to the collapse of soil eco-systems by eliminating soil bacteria and fungi.

- **Resistance**

- Long term or improper use of insecticides can produce resistance in target species.
- In Sri Lanka, parts of India, Pakistan, Turkey and Central America, DDT resistance in mosquitoes has forced a shift to organophosphate and carbamate insecticides for malaria control.

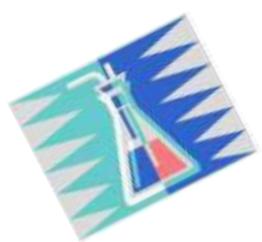




# International Organizations/Agreements concerned with pesticide problems

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

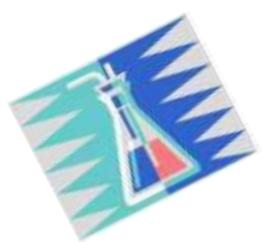




# Current Status

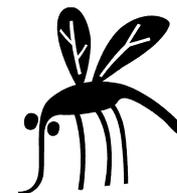
- Large stockpiles of obsolete pesticides are located in many developing countries.
- Many are beyond the manufacturers expiration date.
- Stocks are not inventoried or secured.
- Materials are routinely used by untrained applicators resulting in
  - over application
  - personal exposure
  - contamination of fields, farms, storage facilities and other people.
- <http://www.fao.org/ag/AGP/AGPP/Pesticid/p.htm> has useful information on Pesticide management.

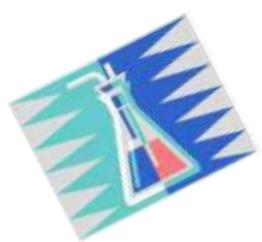




# Pesticide management issues: Global

- **Large stockpiles of pesticides exist as a result of:**
  - **Changes in agricultural/environmental policies in developed nations**
  - **Ratification of several international treaties and conventions.**
  - **These pesticides considered ‘obsolete’ by the FAO.**
- **Many pesticides transferred to the developing world**
  - **Demand exists throughout the developing world**
    - **Especially DDT to combat malaria.**
  - **International manufacturers continue production**
  - **Large amounts of recently banned pesticide products from Europe and North America were freely given to any nation that asked for them.**





# Pesticide management issues: Local

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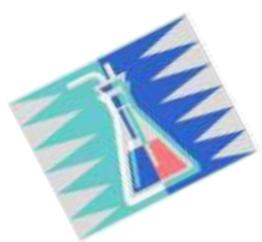
- **Usage**

- Pesticides all come with specific instructions for application.
- Individuals applying these pesticides should be:
  - Well trained
  - Familiar with the inherent hazards posed by these chemicals.
  - Knowledgeable about regional soil conditions and pest organisms.

- **Application**

- Bulk quantities can lack chemical property data and manufacturers instructions on utilization, application and precautions.
- Some pesticide “systems” require the use of special emulsifiers for proper usage.
- Excessive application due to lack of proper instructions occurs frequently.
- Over-application is leading cause of human illness and water/soil contamination/degradation.



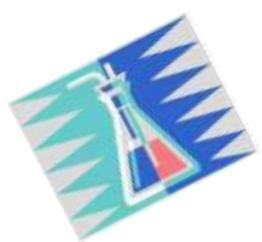


# Pesticide management issues: Local

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- **Storage**

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

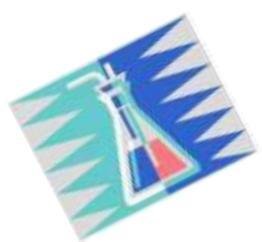


# Pesticide management issues: Local

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- **Disposal**

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



# Obsolete Pesticide Recommendations

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- **Inventory**

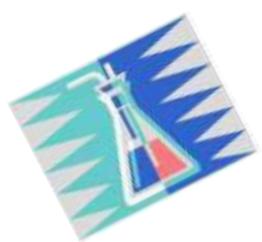
- Many countries do not have central inventory sources
  - Makes it difficult to address the problem of disposal
  - Makes it easier for terrorists to steal pesticides
- What do you have in your country?
  - Who knows the answers?
- Is it usable or deteriorated?
- Do you really need it? Will you really use it?

- **Usable**

- Make safe/secure
- Repackage/re-label if necessary
- Store securely until use by trained personnel

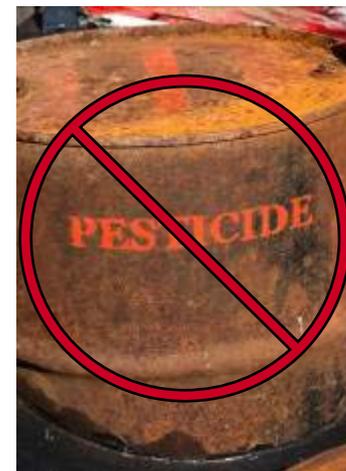
- **Not usable**

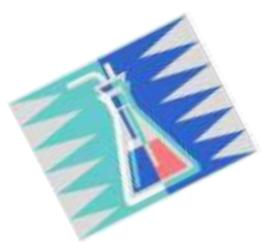
- Make safe/secure
- Repackage/re-label if necessary
- Store securely until proper disposal



# Usable pesticides should be:

- In clean, intact containers
- Appropriately labeled
  - Original manufacturer
  - International labeling standards
- Kept in secure, dry, cool (covered) storage until use.
- Analyzed to determine efficacy
  - If near expiration date
  - Unknown expiration date
  - WHO collaborating center for pesticide analysis can assist.
- Designed for the pest
- Applied by people trained to understand the requirements and hazards involved with the use of these chemicals.
- Applied using the appropriate procedure and equipment
- Applied by people wearing appropriate Personal Protective Equipment (PPE)

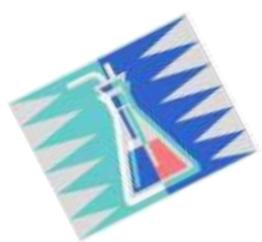




# Unusable pesticides should be:

- Identified whenever possible.
- Secured as part of standard pesticide handling operating procedures.
  - Prevents theft or loss of material
  - Prevents improper application
  - Prevents diversion for nefarious means
- Moved to a dry, covered storage location if the materials are undamaged and identifiable.
- Cleaned up and re-packaged before move to appropriate storage if containers are damaged or labeling unreadable.
- Handled by workers wearing the correct Personal Protective Equipment (coverall, gloves, respirators etc.)
- Stored securely (away from usable stocks) until disposal can be arranged.





# Disposal of Obsolete Pesticide Stocks

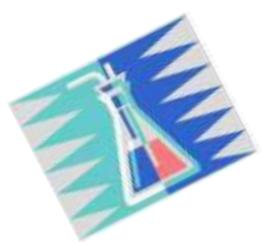
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- **Can be difficult and costly**
- **Currently stored until shipment to facilities that can safely destroy these materials**
  - **High temperature incinerators**
  - **Controlled plasma pyrolysis**
- **Incineration usually considered the best method**
  - **Most countries do not have incinerators that can be used**
  - **Cement kilns are not good for chlorinated pesticides (too low temperatures may cause chlorinated dioxins like those found in Agent Orange to be formed) but may be acceptable for organophosphates and carbamates.**



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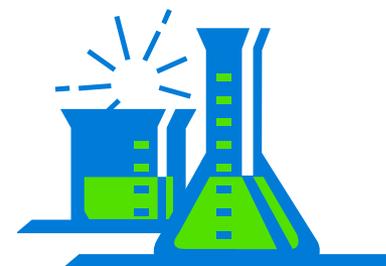
# Chemical Waste Management and Disposal

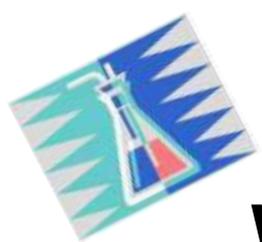


# Waste Management

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

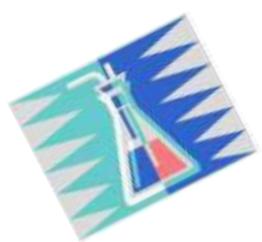




# Waste management: nonhazardous waste

- **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<sub>2</sub>CO<sub>3</sub>)**
- **Sugars - Amino acids**
- **Inert materials (uncontaminated resins and gels)**

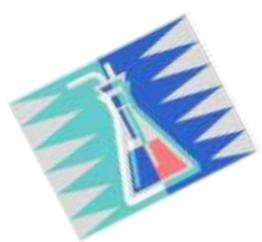




# Waste management: General guidelines

- 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

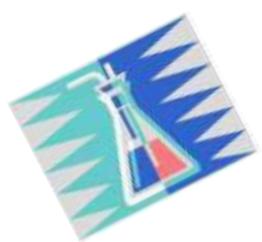




# Waste management: General guidelines

- 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

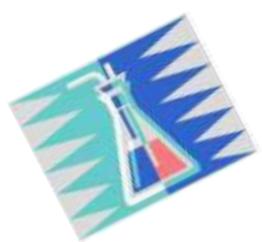




# Waste - Storage guidance

- 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

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



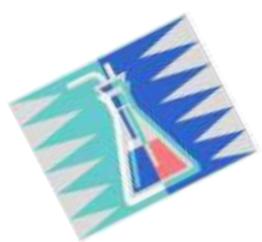
**Pressure can build up in a waste vessel**

**Corrosion can occur in storage vessel**

**Secondary containment is necessary**



**Glass waste containers can break**



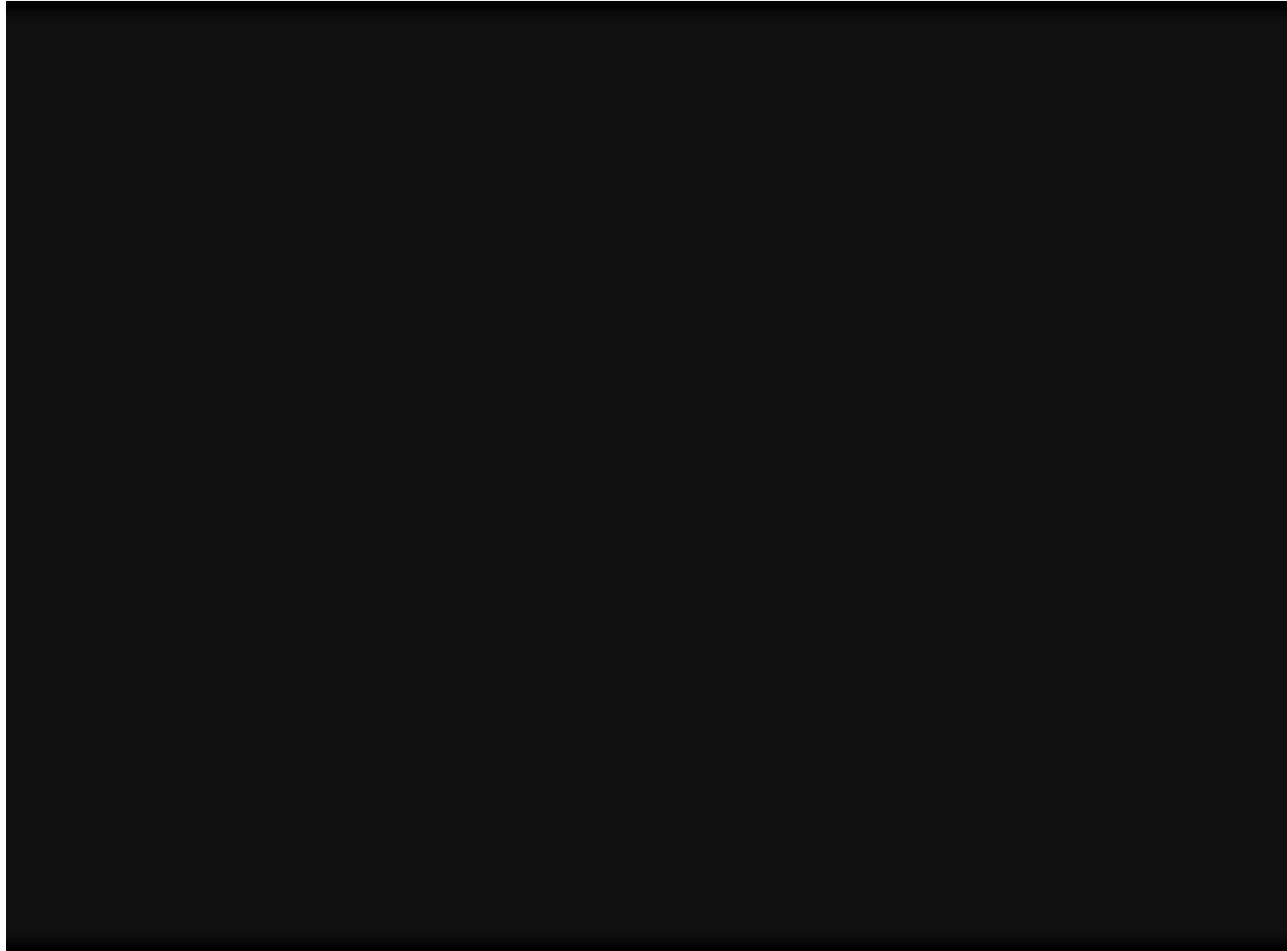
# Dangerous waste management

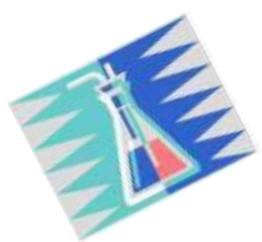




# Video – Fire at Apex Waste Facility

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# Best practice – Orphan control

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**Before moving to new job meet with new lab occupant**

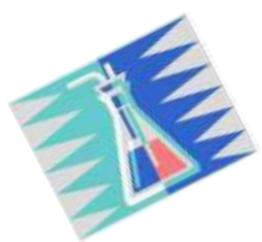
- This can be a new employee or new student
- Label all chemicals and samples carefully
- Make notations in common lab book

**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**

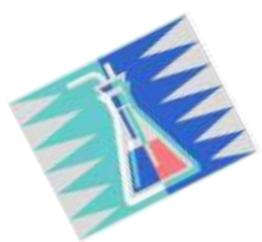


# Waste management

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



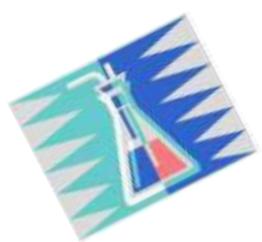


# Emissions from incineration vs. open burning

	Open Burn ( $\mu\text{g}/\text{kg}$ )	Municipal Waste Incinerator ( $\mu\text{g}/\text{kg}$ )
PCDDs	38	0.002
PCDFs	6	0.002
Chlorobenzenes	424150	1.2
PAHs	66035	17
VOCs	4277500	1.2

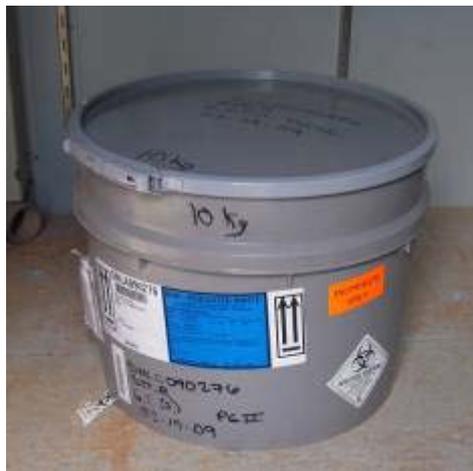


Source: EPA/600/SR-97/134 March 1998

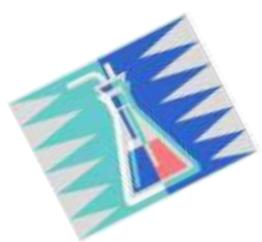


# Laboratory wastes are packaged in small containers

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



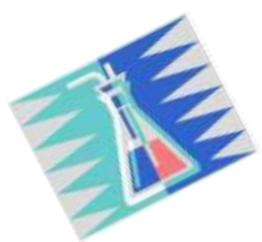
Lab packs segregated at hazardous waste facility



# 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

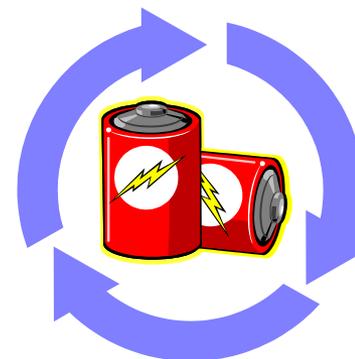




# Battery recycling and disposal

## Hazardous waste

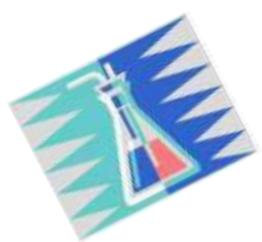
- Lead acid (Pb) - recycle (90% car batteries)
- Sealed lead (Pb) - recycle
- Mercury-oxide (HgO) button, silver-oxide (AgO) button - recycled by jewelers
- Nickel Cadmium (NiCd) recycle



## Nonhazardous waste

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

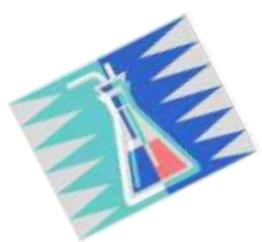




# Mercury metal disposal

- 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)

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**These wastes must be minimized - heavily regulated**

**Universities, hospitals**

**Low level radioactive with chemical**

**Scintillation cocktails**

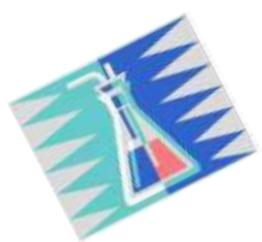
**Gel electrophoresis waste**

**Nuclear energy research**

**Low and high level radioactive with chemical**

**Lead contaminated with radioactivity**



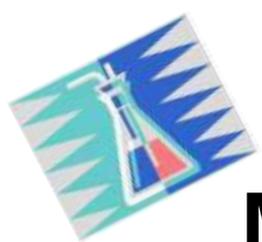


# Mixed Waste (chemical-biological)

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





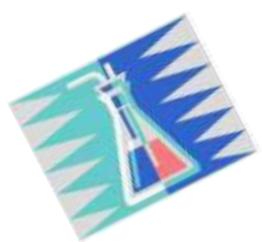
# Mixed Waste (radioactive-biological)

---

## 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**

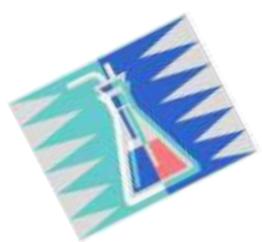
**Air reactivity**

**Water reactivity**

**Flammability**

**Corrosivity**





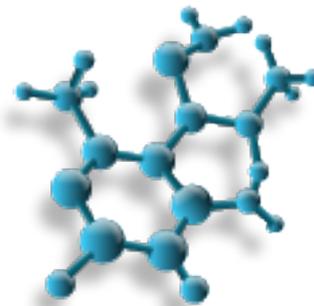
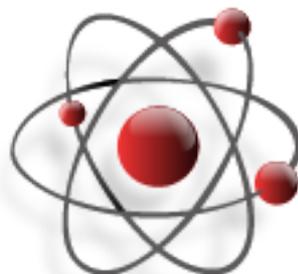
# Unknown waste characterization\*

Physical description - Water reactivity - Water solubility

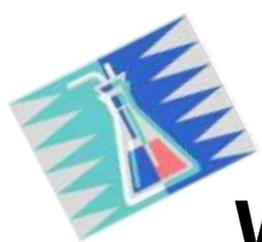
pH and neutralization information

Presence of:

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



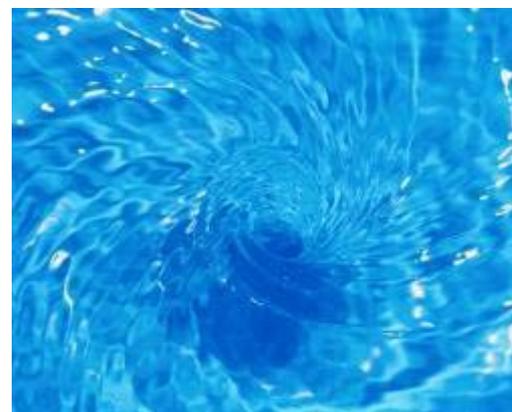
\*Prudent Practices in the Laboratory: Handling and Disposal of Chemicals,” National Academy Press, 1995 Section 7.B.1

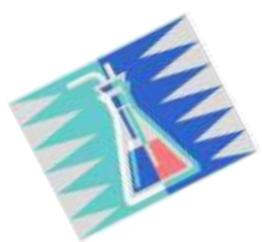


# Waste management: Down the drain?

## 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



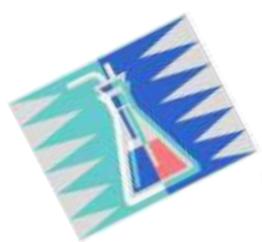
## Adsorption

- 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**

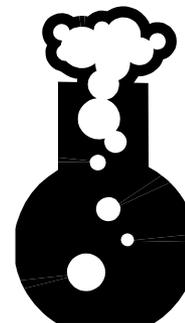
## **Dilution to reduce hazard**

- $\text{H}_2\text{O}_2$ ,  $\text{HClO}_4$ ,  $\text{HNO}_3$
- Never add water to concentrated acid
- Neutralization acid base -gentle

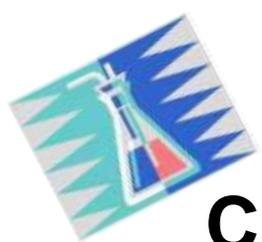
## **Hydrolysis (acid and base)**

- Active halogen compounds with  $\text{NaOH}$
- Carboxamides with  $\text{HCl}$

## **Oxidation-reduction**

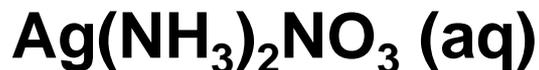


Handbook of Laboratory Waste Disposal, Martin Pitt and Eva Pitt, 1986. ISBN 0-85312-634-8



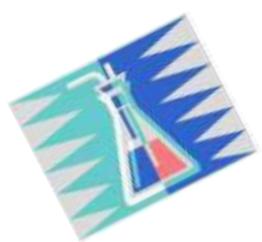
# Chemical Waste Example: Tollens Reagent

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- 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.

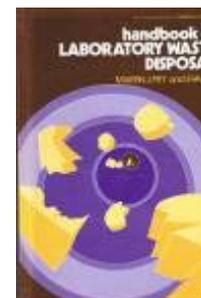
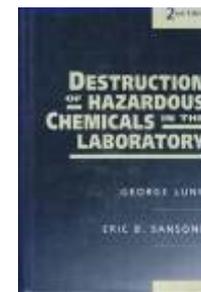
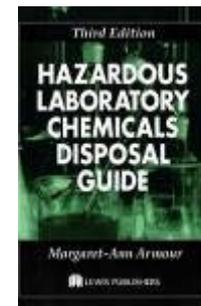




# Waste management: Treatment in Lab

- **References:**

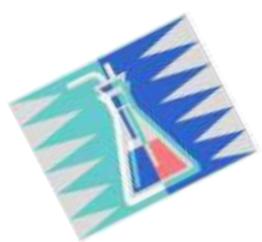
- “Procedures for the Laboratory-Scale Treatment of Surplus and Waste Chemicals, Section 7.D in Prudent Practices in the Laboratory: Handling and Disposal of Chemicals,” National Academy Press, 1995, available online: [http://www.nap.edu/catalog.php?record\\_id=4911](http://www.nap.edu/catalog.php?record_id=4911)
- “Destruction of Hazardous Chemicals in the Laboratory, 2<sup>nd</sup> 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





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# On-site Recycling and Waste Treatment



# Waste Management: Recycling

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**Recycling by redistribution**

**Recycling of metals**

**Gold-mercury-lead-silver**

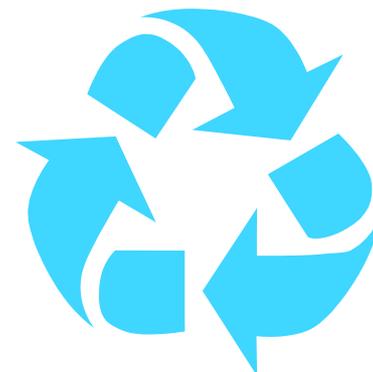
**Recycling of solvents**

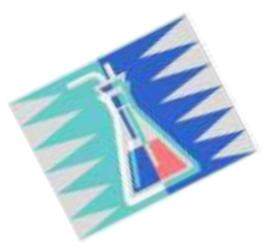
**Clean for reuse-rotovap**

**Distill for purity**

**Recycling of oil**

**Recycling of E-waste**





# Chemical recycling

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**Reuse by others in the organization or community**

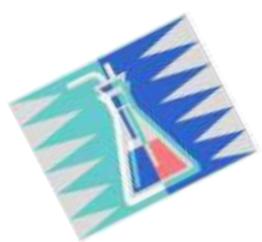
**An active chemical exchange program**

**Beware of accepting unusable chemicals**

**Reuse in experiments in the laboratory**

**Exchange for credit with suppliers by agreement**

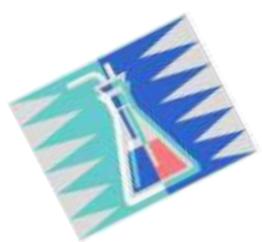




# What should not be recycled

- 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?



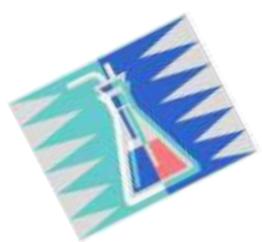


# What should be recycled or redistributed?

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- **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?**

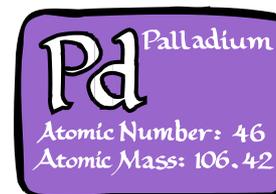




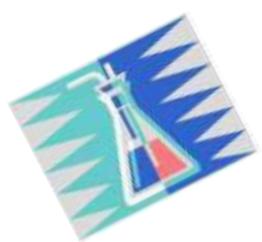
# Chemical Recycling - Precious Metal

For reuse in lab or for exchange

- Requires chemical knowledge for lab reuse
- Recover from solution - evaporate then
  - Ignite (Au, Pd, Pt)
  - Reduce with  $\text{NaBH}_4$  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

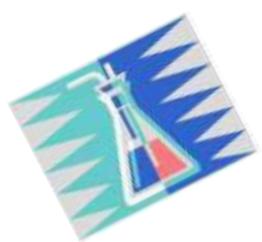
- Acidification and ppt as AgCl

## 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

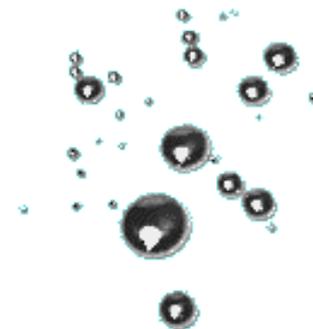
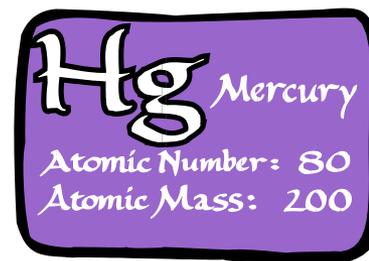
Many companies will buy the recovered silver

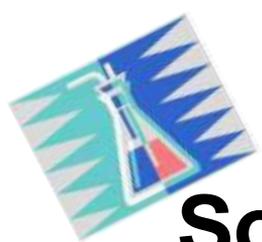




# Chemical Recycling - Mercury

- 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

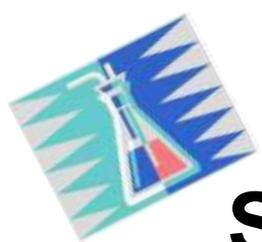




# Solvents can be recovered by distillation

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

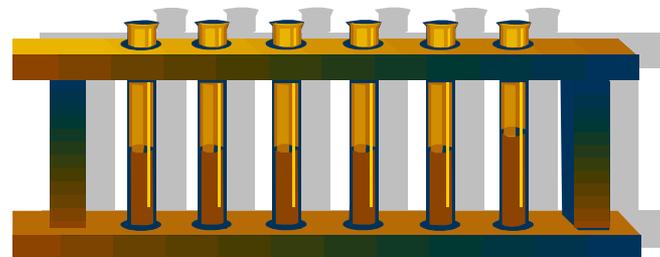


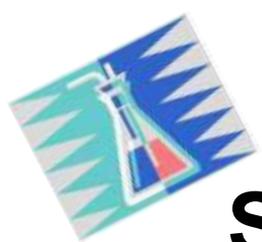


# Solvent recycling – general guidance

## 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**





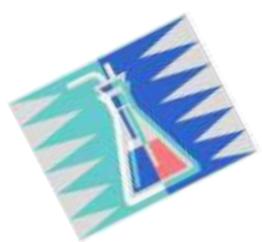
# Solvent recycling – general guidance

## 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  $> 10^{\circ}\text{C}$
- Can form azeotrope\*
  - water / ethanol ( $100^{\circ}\text{C} / 78.3^{\circ}\text{C}$ )
  - cyclohexane / isobutanol ( $81^{\circ}\text{C} / 108^{\circ}\text{C}$ )
- Mixture of 4 solvents not practical
- Distillation can be incorporated into curriculum



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

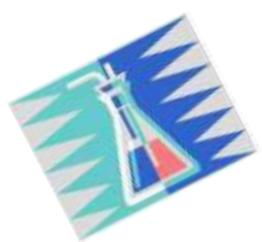


# Solvent recycling – low efficiency

## 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



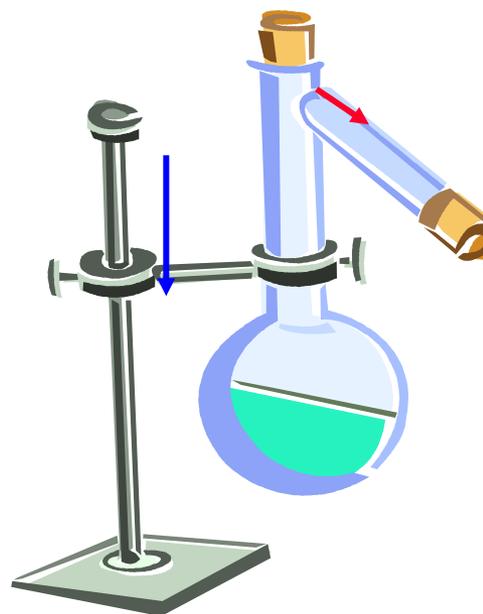


# Solvent recycling – basics

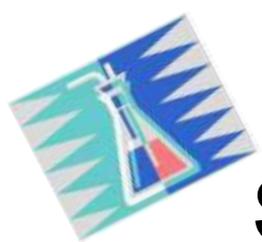
Reflux ratio	TP
120	25
80	24
40	21
20	16
10	10
4	5

**Higher reflux ratio  
leads to increased  
separation efficiency**

TP = theoretical plates



**Reflux**  
**Distillate**



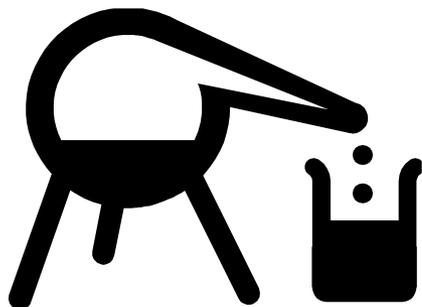
# Solvent recycling – medium efficiency

- 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**

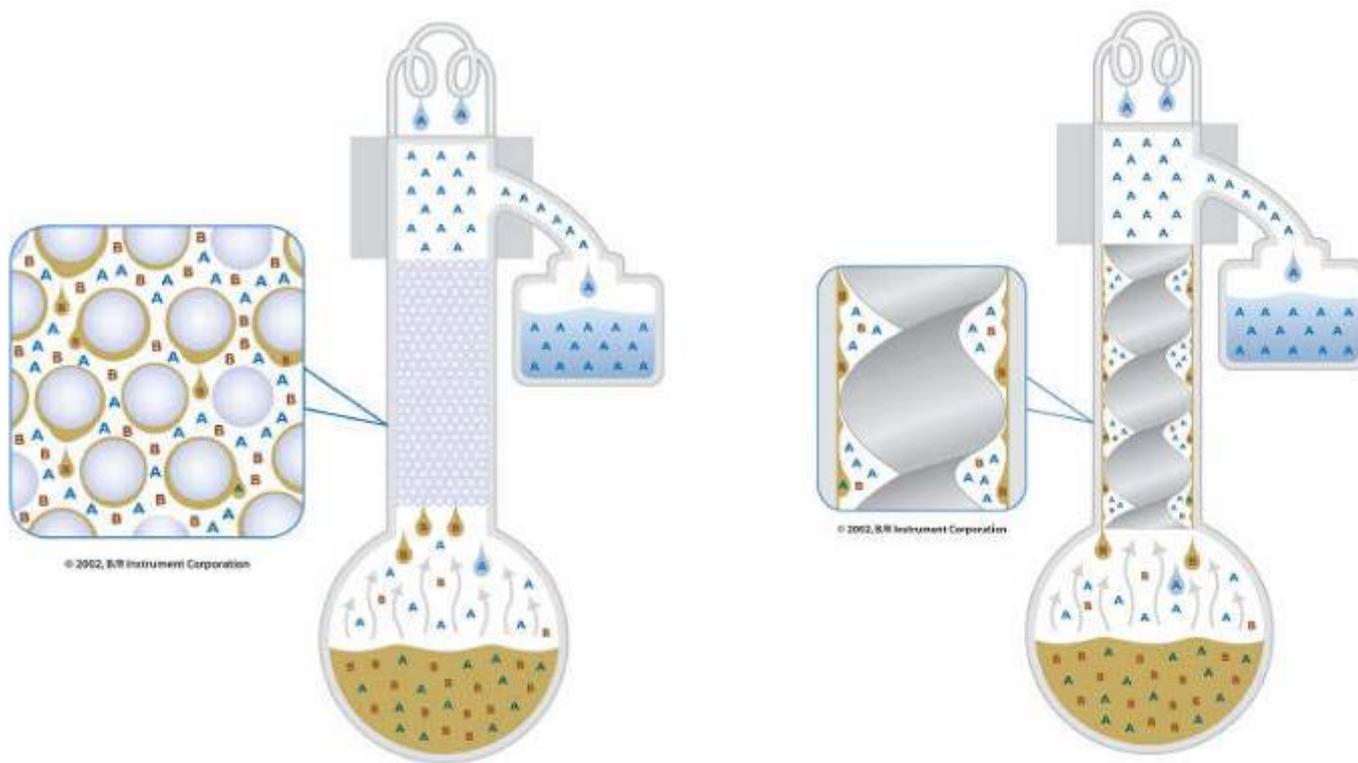
Packing	TP
Empty	0.5
Coarse packing	1
Fine packing	5

TP = theoretical plates

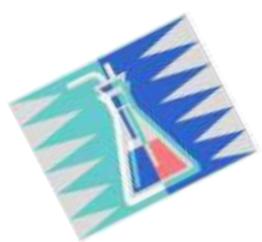




# Diagram of packed and spinning band distillation columns

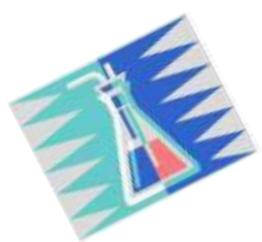


Diagrams from B/R Instruments: <http://www.brinstrument.com/>



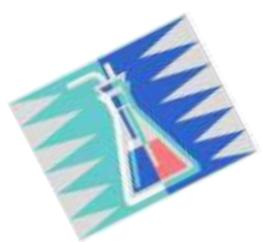
# Boiling point of common solvents (C)

Halogen Containing		
Dichloromethane	40	$\text{CH}_2\text{Cl}_2$
Chloroform	61.6	$\text{CH}_3\text{Cl}$
Carbontetrachloride	76.5	$\text{CCl}_4$
Trichloroethane	87	$\text{C}_2\text{H}_3\text{Cl}_3$
Perchloroethylene or Tetrachloroethylene	121	$\text{C}_2\text{Cl}_4$
Trichloroethylene	87	$\text{C}_2\text{HCl}_3$
Trichlorobenzene (TCB)	208.5	$\text{C}_6\text{H}_3\text{Cl}_3$



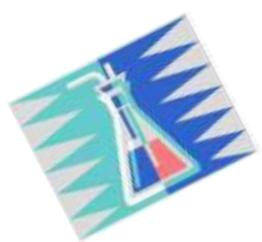
# Boiling point of common solvents (C)

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	$C_6H_{12}O$



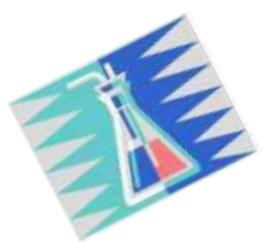
# Boiling point of common solvents (C)

Oxygen Containing (cont)		
Methanol	64.5	CH <sub>4</sub> O
Ethanol	78.3	C <sub>2</sub> H <sub>6</sub> O
n-Propanol	97	C <sub>3</sub> H <sub>8</sub> O
Isopropanol	82.5	C <sub>3</sub> H <sub>8</sub> O
n-Butanol	117.2	C <sub>4</sub> H <sub>10</sub> O
sec-Butanol	99.5	C <sub>4</sub> H <sub>10</sub> O



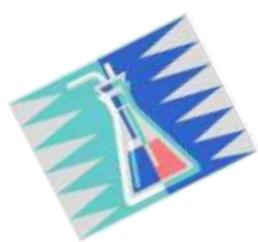
# Boiling point of common solvents (°C)

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-Methylpyrrolidone	202	$C_5H_9NO$
Piperdine	106	$C_5H_{11}N$
Acetonitrile	81.6	$C_2H_3N$



# Solvents that should not be recycled by distillation

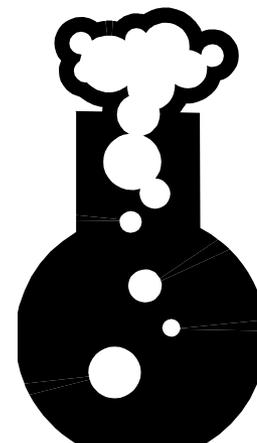
**Accidents have been reported for these distillations**

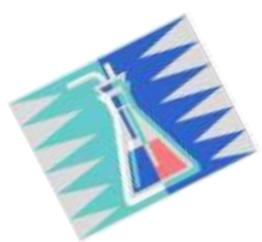
## Individual Substances

- 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



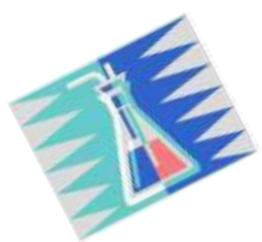


# Practical examples of recycling

- 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**

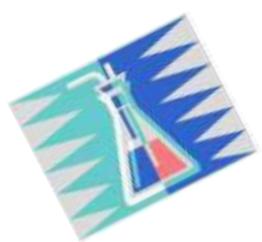
**Freon Solvent Recycling**

**Histology Laboratory Solvent Recycling**

**General Lab Solvent Recycling Services Can also be Purchased**



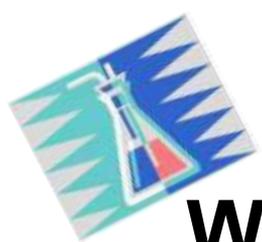
Pictures from B/R Instruments: <http://www.brinstrument.com/>



# Any Questions?

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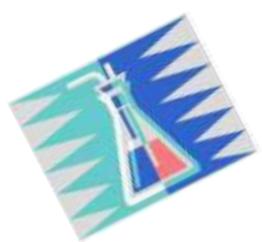


# Workshop evaluation and feedback form

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





# Thanks!

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## Videos:

- Chemical Safety Board
- Washington State Emergency Management Division, Public Education Program
- US Army Research, Development and Engineering Command