

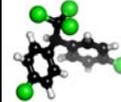


Chemical Safety and Security Officer Training

Algeria
December 2011



SAND No. 2009-636P
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.

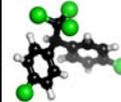


Lab Visit

2



Lunch



Chemical Waste Management and Disposal

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Waste Management

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




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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, Na₂CO₃)
- Sugars – Amino acids
- Inert materials (uncontaminated resins and gels)




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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







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Waste management: General guidelines

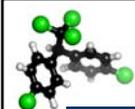
- Insure against leakage; dyke area if possible
- Label all chemicals, containers, vials
- Separate incompatible chemicals
- Keep gas cylinders separate
- Keep radioactive material separate
- Know how long waste can be stored
- Provide for timely pick-up




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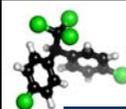
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Waste Storage guidance

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



Waste – General guidance

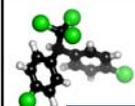
Certain metals cause disposal problems when mixed with flammable liquids or other organic liquids

Pressure can build up in a waste vessel

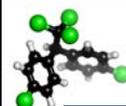
Corrosion can occur in storage vessel

Secondary containment is necessary

Glass waste containers can break

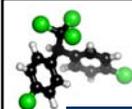


Dangerous waste management



Video – Fire at Apex Waste Facility





Best practice – Orphan control

Before moving to new job meet with new lab occupant

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

Dispose of all unneeded or excess chemicals

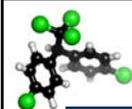
- Put into chemical exchange program
- Dispose of as hazardous waste



Do not leave any chemicals behind except by agreement



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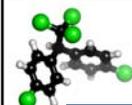


Waste management

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



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Emissions from incineration vs. open burning

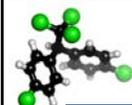
	Open Burn ($\mu\text{g}/\text{kg}$)	Municipal Waste Incinerator ($\mu\text{g}/\text{kg}$)
PCDDs	38	0.002
PCDFs	6	0.002
Chlorobenzenes	424150	1.2
PAHs	66035	17
VOCs	4277500	1.2



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



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Lab wastes are packaged in small containers

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

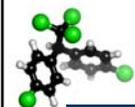


Lab packs segregated at hazardous waste facility



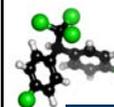
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Waste management: Waste disposal service

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



Battery recycling and disposal

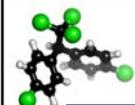
Hazardous waste

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



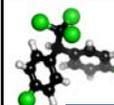
Nonhazardous waste

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



Mercury metal disposal

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



Mixed Waste (chemical radioactive)

These wastes must be minimized – heavily regulated

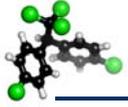
Universities, hospitals

- Low level radioactive with chemical
- Scintillation cocktails
- Gel electrophoresis waste



Nuclear energy research

- Low and high level radioactive with chemical
- Lead contaminated with radioactivity



Mixed Waste (chemical–biological)

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




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Mixed Waste (radioactive–biological)

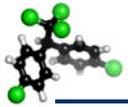
Medical wastes

- 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 allowed (sharps as well)




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Unknown “orphan” waste

Avoid if at all possible – requires analysis before disposal!

Pre–screen:

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

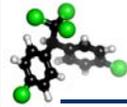
Screen:

- Prepare for the worst: wear gloves, goggles, use hood
- Check for: Air reactivity, Water reactivity, Flammability, Corrosivity



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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

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Chemical SAFETY AND SECURITY TRAINING

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




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Chemical SAFETY AND SECURITY TRAINING

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

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Chemical SAFETY AND SECURITY TRAINING

Treating on site – chemical conversion

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

Dilution to reduce hazard

- H₂O₂, HClO₄, HNO₃
- 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

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Chemical SAFETY AND SECURITY TRAINING

Chemical Waste Example: Tollens Reagent

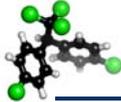
Ag(NH₃)₂NO₃ (aq)

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



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Chemical Waste Example: Sodium Cyanide

- Wear PPE, work in hood
- Add sodium cyanide to a solution of 1% sodium hydroxide (~50mL/g of cyanide).
- Household bleach (~70mL/g of cyanide) is slowly added to the basic cyanide solution while stirring.
- When addition of the bleach is complete, test for the presence of cyanide using the Prussian blue test:
 - To 1mL of the solution to be tested, add 2 drops of a freshly prepared 5% aqueous ferrous sulfate solution.
 - Boil this mixture for at least 60 seconds, cool to room temperature, then add 2 drops of 1% ferric chloride solution.
 - Take the resulting mixture, make it acid (to litmus paper) using 6M hydrochloric acid.
 - If cyanide is present, a deep blue precipitate will be formed.
- If test is positive, add more bleach, then retest.




From "Hazardous Laboratory Chemicals Disposal Guide", Armour, 2003.

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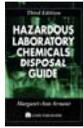
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Waste management: Treatment in Lab

- ▶ References:
 - "Procedures for the Laboratory-Scale Treatment of Surplus and Waste Chemicals, Section 7.D in Prudent Practices in the Laboratory: Handling and Disposal of Chemicals," National Academy Press, 1995, available online:
http://www.nap.edu/catalog.php?record_id=4911
 - "Destruction of Hazardous Chemicals in the Laboratory, 2nd Edition", George Lunn and Eric B. Sansone, Wiley Interscience, 1994, ISBN 978-0471573999.
 - "Hazardous Laboratory Chemicals Disposal Guide, Third Edition", Margaret-Ann Armour, CRC Press, 2003, ISBN 978-1566705677
 - "Handbook of Laboratory Waste Disposal", Martin Pitt and Eva Pitt, 1986. ISBN 0-85312-634-8





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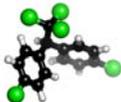


Break

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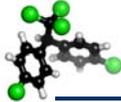


On-site Recycling and Waste Treatment

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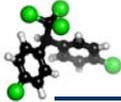
Waste Management: Recycling

- 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



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Chemical SAFETY AND SECURITY TRAINING



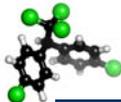
Chemical recycling

- 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




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Chemical SAFETY AND SECURITY TRAINING



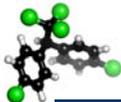
What should not be recycled

- 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?



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Chemical SAFETY AND SECURITY TRAINING



What should be recycled or redistributed?

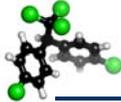
- Excess unopened chemicals
- Excess laboratory glassware (unused or clean)
- Consumables with no expiration
- Solvent that can be purified
 - Lower purity suitable for secondary use?
- Precious or toxic metals
 - Hg, Ag, Pt, Pd, Au, Os, Ir, Rh, Ru
- Others?



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Chemical SAFETY AND SECURITY TRAINING

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

Au Gold
Atomic Number: 79
Atomic Mass: 196.97

Pt Platinum
Atomic Number: 78
Atomic Mass: 195.02

Pd Palladium
Atomic Number: 46
Atomic Mass: 106.42

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


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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

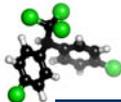
Many companies will buy the recovered silver

Ag Silver
Atomic Number: 47
Atomic Mass: 107.87




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Chemical Recycling – Mercury



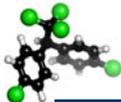
- Mercury can be recovered for subsequent lab use or for recycle by vendor
- Remove particulates and moisture by allowing slow drip through a hole in a conical filter paper
- Never distill Hg on-site

Hg Mercury
Atomic Number: 80
Atomic Mass: 200




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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

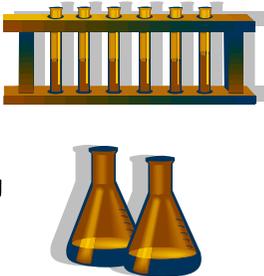



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Solvent recycling – general guidance

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



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Chemical SAFETY AND SECURITY TRAINING

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



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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



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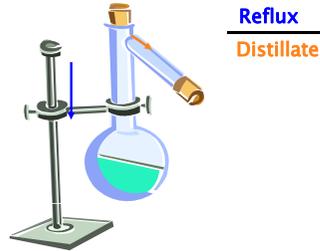
Chemical SAFETY AND SECURITY TRAINING

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

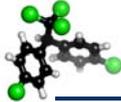


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Chemical SAFETY AND SECURITY TRAINING



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



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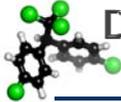
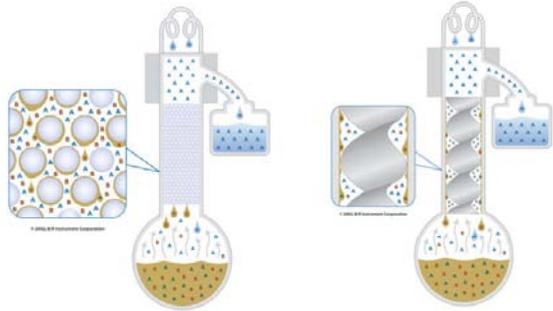


Diagram of packed and spinning band distillation columns

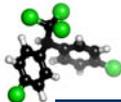


Diagrams from B/R Instruments: <http://www.brinstrument.com/>

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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

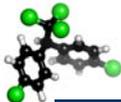
- Chloroform + acetone
- Any ether + any ketone
- Isopropyl alcohol + any ketone
- Any nitro compound + any amine



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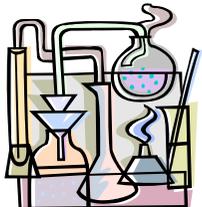
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Chemical SAFETY AND SECURITY TRAINING



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

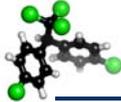


Source: Handbook of Laboratory Waste Disposal, 1986. Marion Pitt and Eva Pitt, John Wiley and Sons, ISBN 85312-634-8

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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

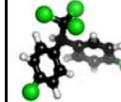
Can also be Purchased




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

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Open Discussion:

Next Steps:

- Priorities
- Teams/partners
- Timelines

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Evaluation Form

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Feedback Form

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Adjourn

