Chemical Safety and Security Officer Training

Yemen
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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

Lunch

Chemical Waste Management and Disposal

Waste Management

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

Waste management: Nonhazardous Waste

- Used oil (uncontaminated) is not considered hazardous waste. Label Containers "USED OIL", not "hazardous waste."
- Uncontaminated PPE (gloves, wipes)
- Triply rinsed glassware (bottles, droppers, pipettes)
- Salts (KCl, NaCl, Na_2CO_3)
- Sugars – Amino acids
- Inert materials (uncontaminated resins and gels)

Waste management: General Guidelines

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

Waste management: General guidelines

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

Waste Storage guidance

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

Waste – General guidance

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

Pressure can build up in a waste vessel

Corrosion can occur in storage vessel

Secondary containment is necessary

Glass waste containers can break

Dangerous waste management

Video – Fire at Apex Waste Facility

Best practice – Orphan control

Before moving to new job meet with new lab occupant
- This can be a new employee or new student
- Label all chemicals and samples carefully
- Make notations in common lab book

Dispose of all unneeded or excess chemicals
- Put into chemical exchange program
- Dispose of as hazardous waste

Do not leave any chemicals behind except by agreement

Waste management

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

Emissions from incineration vs. open burning

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

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

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

Waste management: Waste disposal service

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

Battery recycling and disposal

Hazardous waste

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

Nonhazardous waste

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

Mercury metal disposal

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

Mixed Waste (chemical radioactive)

These wastes must be minimized – heavily regulated

Universities, hospitals

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

Nuclear energy research

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

Mixed Waste (chemical-biological)

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

Mixed Waste (radioactive-biological)

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

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)

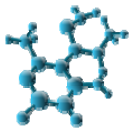
Screen:
- Prepare for the worst: wear gloves, goggles, use hood
- Check for: Air reactivity, Water reactivity, Flammability, Corrosivity

Unknown waste characterization*

Physical description – Water reactivity – Water solubility

pH and neutralization information

Presence of:
- ✓ Oxidizer
- ✓ Sulfides or cyanides
- ✓ Halogens
- ✓ Radioactive materials
- ✓ Biohazards
- ✓ Toxics

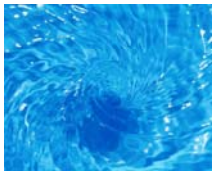


*Prudent Practices in the Laboratory: Handling and Disposal of Chemicals," National Academy Press, 1995 Section 7.B.1

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



On-site Recycling and Waste Treatment

Waste Management: Recycling

Recycling by redistribution

Recycling of metals

Gold-mercury-lead- silver

Recycling of solvents

Clean for reuse-rotovap

Distill for purity

Recycling of oil

Recycling of E-waste

Chemical recycling

Reuse by others in the organization or community

An active chemical exchange program
Beware of accepting unusable chemicals

Reuse in experiments in the laboratory

Exchange for credit with suppliers by agreement

What should not be recycled

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

What should be recycled or redistributed?

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

Chemical Recycling – Precious Metal

For reuse in lab or for exchange

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

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

Chemical Recycling – Silver

Recovery from chemical oxygen demand (COD) test

- Acidification and ppt as AgCl

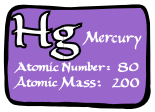
Recovery from photographic fixing solution

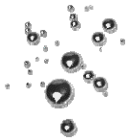
- Precipitate as sulfide
- Precipitate with TMT (trimercapto-s-triazine)
- Electrolysis (terminal and in-line)
- Metal replacement (iron containing cartridges)
- Ion exchange

Many companies will buy the recovered silver

Chemical Recycling – Mercury

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





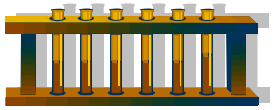
Solvents can be recovered by distillation

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

Solvent recycling – general guidance

Solvent recycling requires care and organization

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



Solvent recycling – general guidance

Solvent recycling requires care and organization

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

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

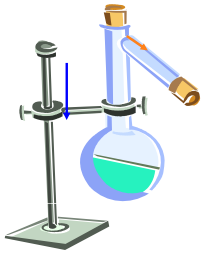
Solvent recycling – low efficiency

Rotovap can be used to pretreat

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

Solvent recycling – basics

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



Reflux / Distillate

Higher reflux ratio leads to increased separation efficiency

TP = theoretical plates

Solvent recycling – medium efficiency

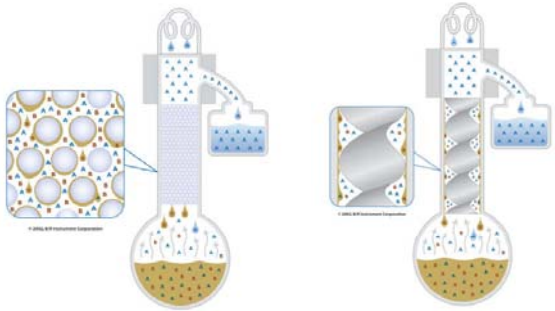
- Even high efficiency stills are not perfect
- Continuous better than batch for large volumes
- Control reflux
- Monitor head temperature
- Reduce heat loss to get more efficiency
- Do not let still operate to dryness
- Use boiling chips but do not add when solvent is hot

Example: 200mm long column for separating benzene and toluene

Packing	TP
Empty	0.5
Coarse packing	1
Fine packing	5

TP = theoretical plates

Diagram of packed and spinning band distillation columns

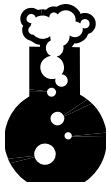


Diagrams from B/R Instruments: http://www.brinstrument.com/

Solvents that should not be recycled by distillation

Accidents have been reported for these distillations

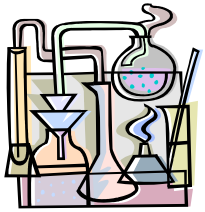
Individual Substances
- Di-isopropyl ether (isopropyl alcohol)
- Nitromethane
- Tetrahydrofuran
- Vinylidene chloride (1,1 dichloroethylene)



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/

Treating on site – Volume Reduction

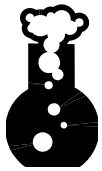
Evaporation – if not excessive
- Roto evaporation for recovery
- Do not evaporate corrosives or radioactives
- Only in laboratory hood
- Beware toxics and flammables

Adsorption
- Activated carbon
- Ion exchange resin
- Activated alumina

Precipitation – Extraction

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

Treating on site – chemical conversion



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

Dilution to reduce hazard
- H_2O_2, $HClO_4$, HNO_3
- Never add water to concentrated acid
- Neutralization acid base –gentle

Hydrolysis (acid and base)
- Active halogen compounds with NaOH
- Carboxamides with HCl

Oxidation–reduction

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

Chemical Waste Example: Tollens Reagent

$Ag(NH_3)_2NO_3$ (aq)

- The reagent should be freshly prepared and stored refrigerated in a dark glass container. It has a shelf-life of ~24 hours when stored in this way.

- After the test has been performed, the resulting mixture should be acidified with dilute acid before disposal. These precautions are to prevent the formation of the highly explosive silver nitride.

Waste management: Treatment in Lab

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

Lab Safety & Security Activity:

What's Wrong With These Pictures?

What's Wrong With This Picture?

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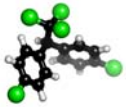
Break

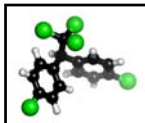
Open Discussion:

Next Steps:

- Priorities
- Teams/partners
- Timelines



Feedback Form



Adjourn