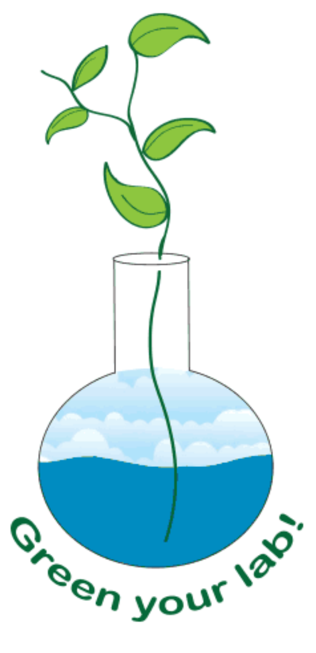
Partnering for Hazardous Waste Minimization at CU-Boulder



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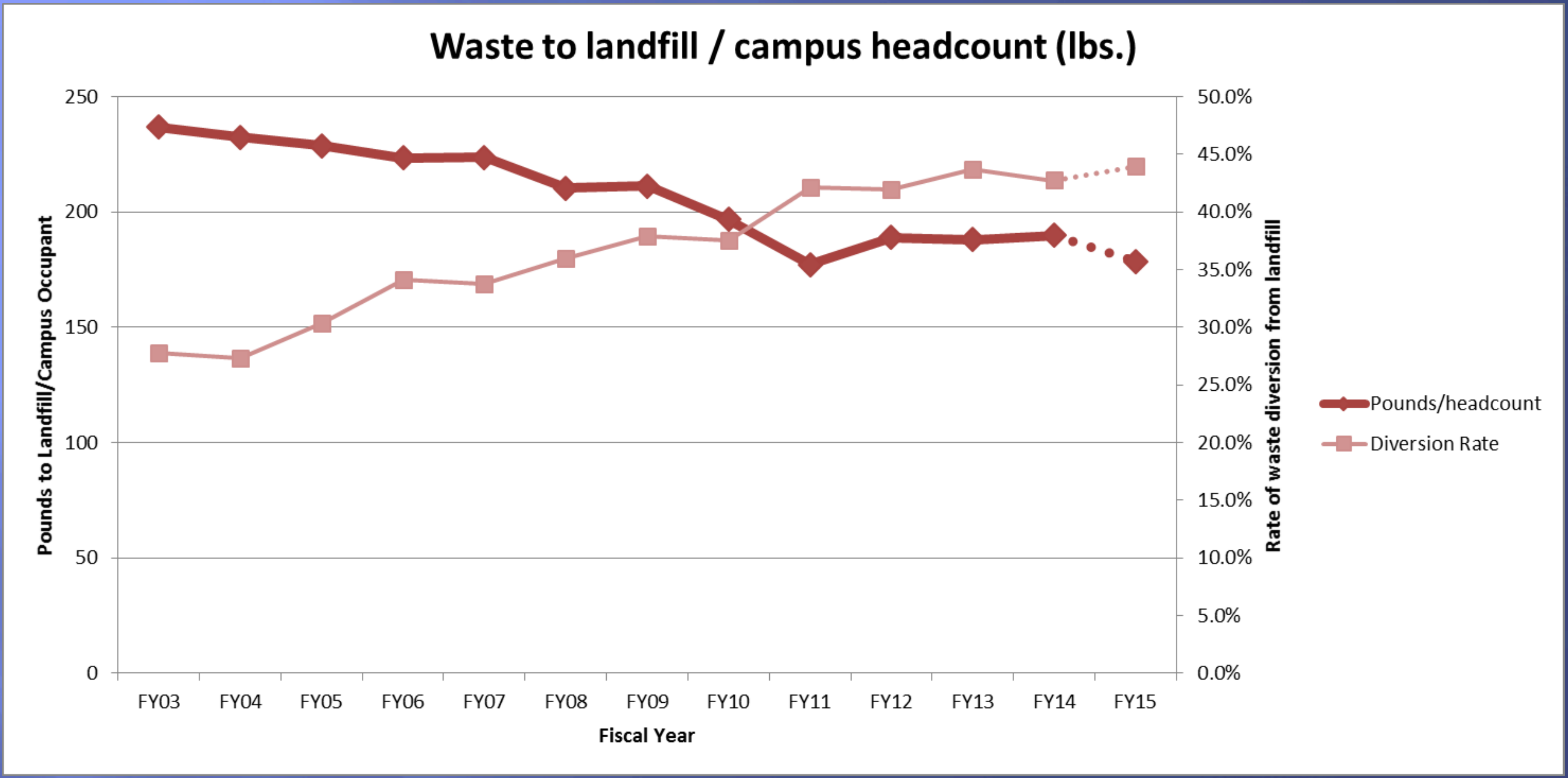
Municipal Waste Diversion

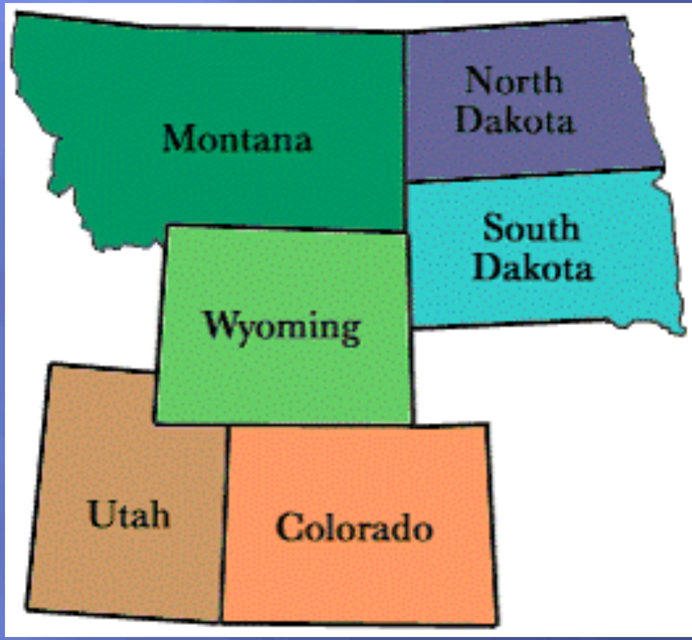


Barriers to Haz. Waste Minimization

- Special hazards and great diversity
- Different wastes between disciplines
- Wastes within a single lab will change depending on projects
- Purity/contamination concerns for reuse
- Funding – we haul it away for free (usually)

Treatment Storage and Disposal Facility (TSDF)

Our TSDF is 1 of only 2 at a University in EPA Region 8



Consolidation

The T in TSDF

Chemical Treatment Facility

Treated Wastes

- Photographic wastes
  - Ion Exchange to recover Silver
- Trace Organic wastes
  - Oxidation using ozone
- Corrosive wastes: Acids and Bases
  - Elementary Neutralization

Treatment Totals Since 2001

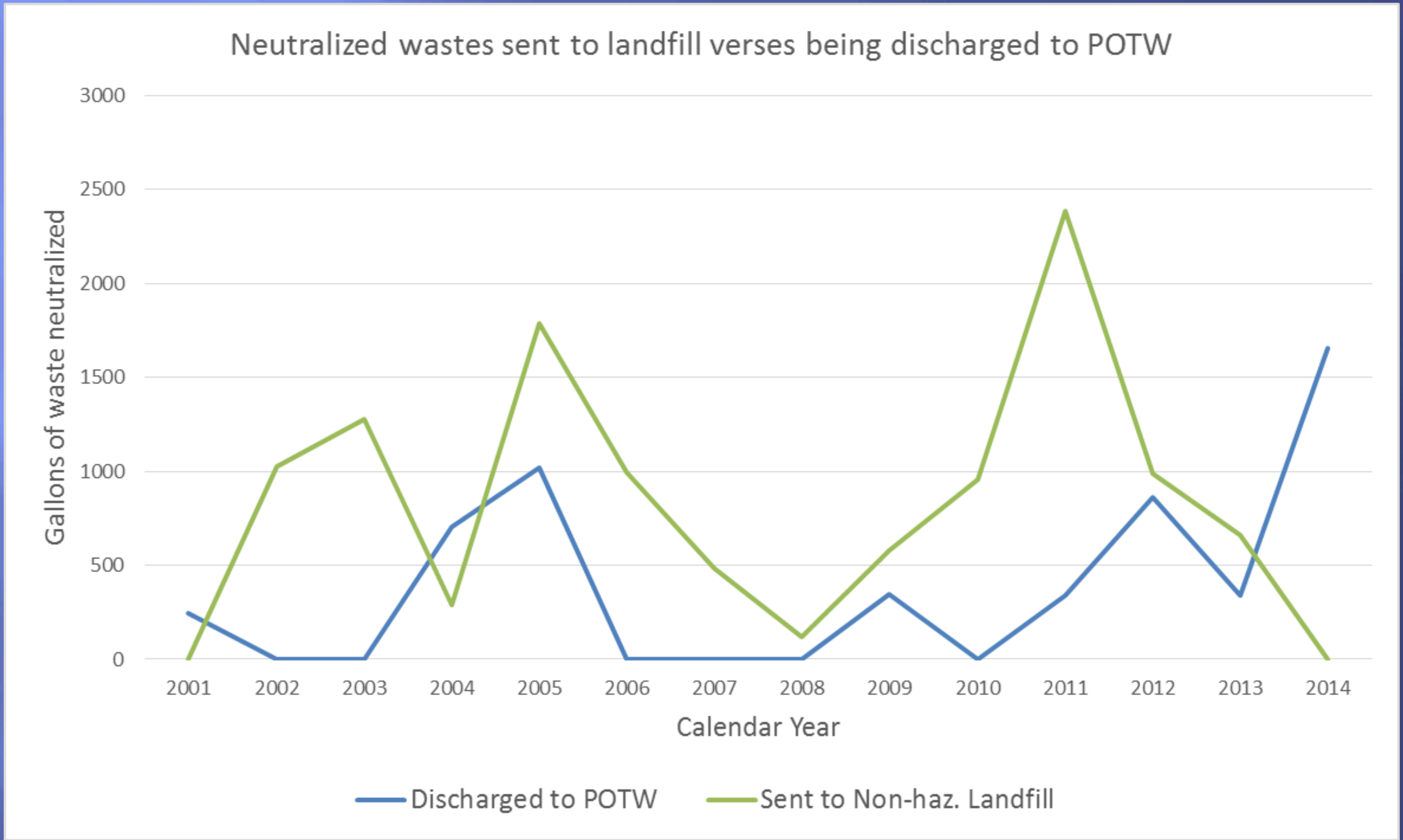
Type of Waste	Volume (gallons)
Photo	44,984
Neutralization	14,036
Oxidation	4,836
Total	63,856

Or as 55 gallon drums = 1,161

Neutralization Equipment

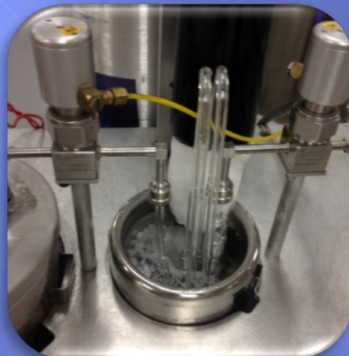
Trace Metals Removal

100% Discharge Rate for Neutralized Wastes!



Ethanol Reuse

Cold trap ethanol



Hazardous waste

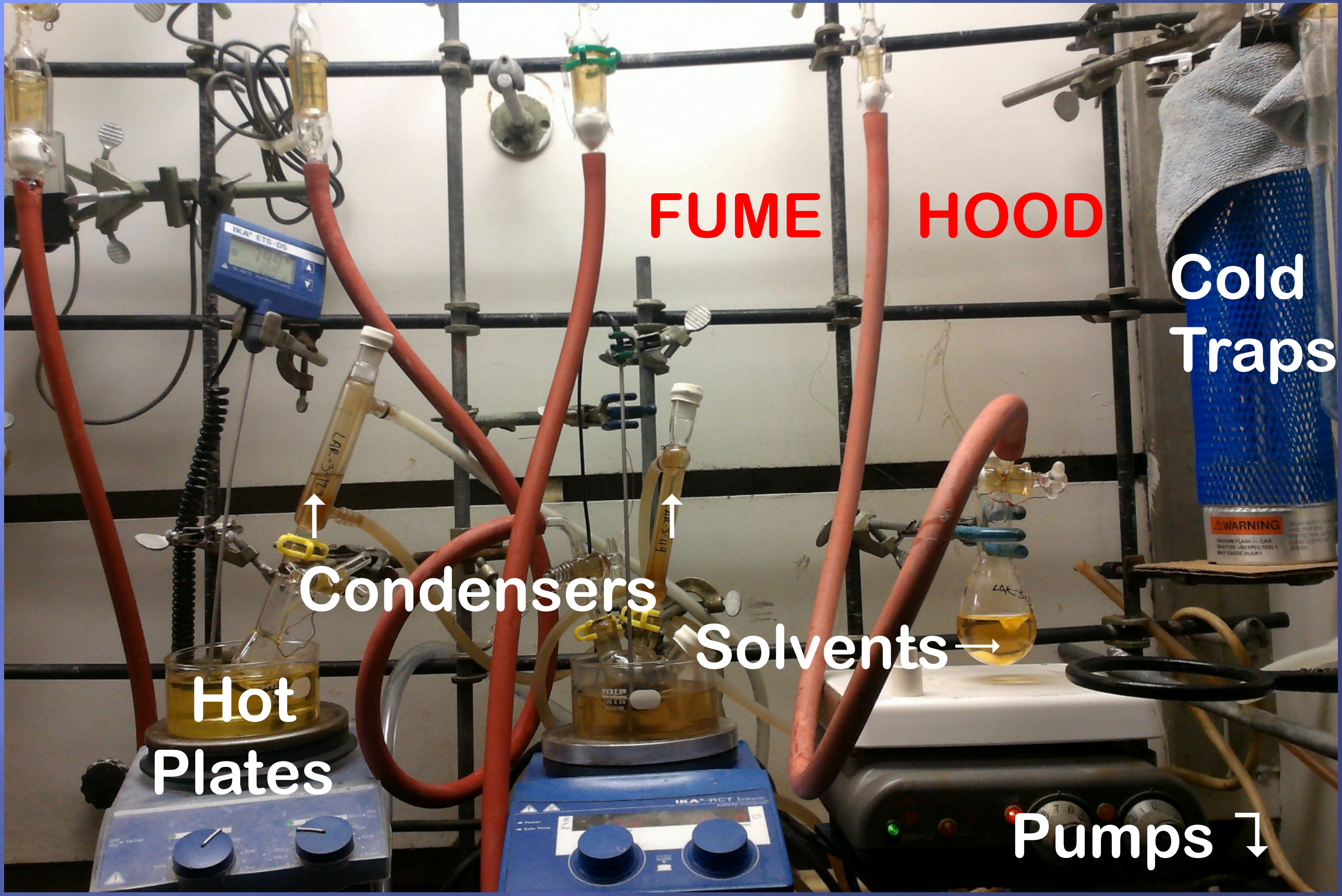
Clean trap ethanol to be diluted to 70%

Ethanol spray & wipe of Biosafety Cabinets

Ethanol Reuse

- ❖ Reducing haz waste
- ❖ Saving $ for Cell Culture
  - ➢ 120 gal/yr x $13/gal= $1560/yr
- ❖ Required a teamwork approach
  - ➢ Scientist reaching out
  - ➢ EH&S & CU Green Labs think of solution
  - ➢ CU Green Labs engages Cell Culture, creates signage, & works with EH&S to set up system
  - ➢ EH&S ongoing transport of materials

Green Chemistry in Research Labs



Green Chemistry in Research Labs

- Materials goods that make the chemistry
  - Research funding
  - Water & energy
  - Brown glass bottles & metal cans for transport and dispersion of solvents & reagents
  - Clean dishes (waste generation, i.e., acetone)
  - Purification (more waste generation)
  - Specialized reagents (i.e., metal catalysts)
  - Disposal of generated waste

…To name a few…

Acetone Recycling

- ❖ Idea: Distill glassware "rinse" acetone for reuse
- ❖ Team Approach Required:
  - ➢ Grant written by Chemistry Green Labs Team Lead
  - ➢ Matching funds - Chemistry, FacMan, EH&S, & Zero Waste SAT
  - ➢ Labs collect "rinse" acetone
  - ➢ Chemistry committed to process acetone & maintain/repair
  - ➢ EH&S installed unit, set-up collection site & procedures, gave training, and transports acetone where necessary

Acetone Recycling: How It Works

Rinse acetone from undergrad and grad labs

Separate rinse acetone waste collection

Added to recycler

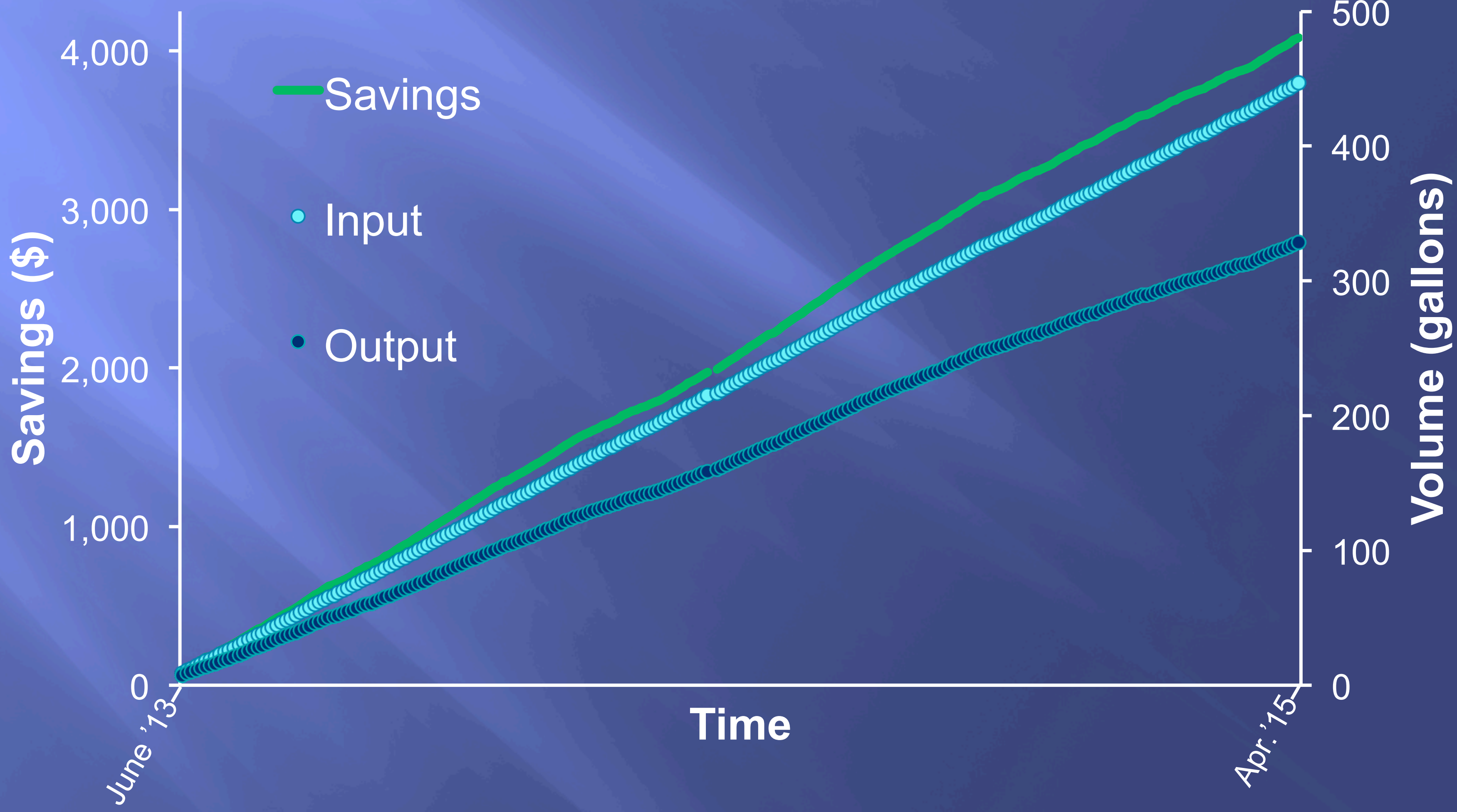
Clean, fractionally distilled acetone

Leftover H_2O, salts, etc.

Disposed of as hazardous waste

Acetone Recycling: Savings

❖ **Overall efficiency = 73.1%; overall savings = $4,084***



*** Not including previous disposal costs**

Other Recycling

- Current recycling
  - Carboy (Cristol Chemistry)
  - Plastic film, pipette tip box, Styrofoam (JSCBB)
- In progress
  - Metal, select brown glass bottles

Carboys

Metal Reagent Cans & Solvent Drums

Brown Glass

Solvent Substitutions

- A number of solvent selection guides are available from industry

Glaxo-Smith Kline (GSK)

	Few issues (bp°C)	Some issues (bp°C)	*Major* issues
Chlorinated	....before using chlorinated solvents, have you considered TBME, isopropyl acetate, ethyl acetate, 2-Methyl THF or Dimethyl Carbonate?		Dichloromethane ** Carbon tetrachloride ** Chloroform ** 1,2-Dichloroethane **
Greenest Option	Water (100°C)		
Alcohols	1-Butanol (118°C) 2-Butanol (100°C)	Ethanol/IMS (78°C) t-Butanol (82°C) 1-Propanol (97°C) 2-Propanol (82°C) Methanol (65°C)	2-Methoxyethanol **
Esters	t-Butyl acetate (95°C) Isopropyl acetate (89°C) Propyl acetate (102°C) Dimethyl Carbonate (91°C)	Ethyl acetate (77°C) Methyl acetate (57°C)	
Ketones		Methyl isobutyl ketone (117°C) Acetone (56°C)	Methyl ethyl ketone
Aromatics		p-Xylene (138°C) Toluene ** (111°C)	Benzene **
Hydrocarbons		Isooctane (99°C) Cyclohexane (81°C) Heptane (98°C)	Petroleum spirit ** 2-Methylpentane Hexane
Ethers		t-Butyl methyl ether (55°C) 2-Methyl THF (78°C) Cyclopentyl methyl ether (106°C)	1,4-Dioxane ** 1,2-Dimethoxyethane ** Tetrahydrofuran Diethyl ether Diisopropyl ether **
Dipolar aprotics		Dimethyl sulfoxide (189°C)	Dimethyl formamide ** N-Methyl pyrrolidone ** N-Methyl formamide ** Dimethyl acetamide ** Acetonitrile

** = EHS Regulatory Alerts: please consult the detailed solvent guide and the GSK Chemicals Legislation Guide for more information http://solventguide.gsk.com/

GSK SSG-MC-02 September 2010

Green Chem. **2011**, *13*, 854–862.

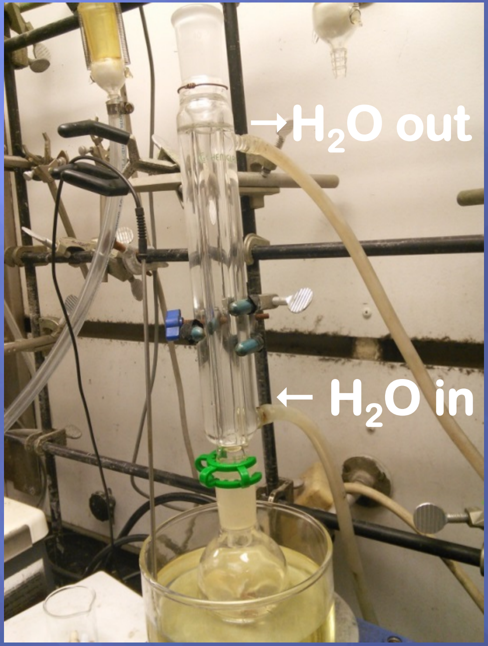
Pfizer

Preferred	Usable	Undesirable
Water	Cyclohexane	Pentane
Acetone	Heptane	Hexane(s)
Ethanol	Toluene	Di-isopropyl ether
2-Propanol	Methylcyclohexane	Diethyl ether
1-Propanol	TBME	Dichloromethane
Ethyl Acetate	Isooctane	Dichloroethane
Isopropyl acetate	Acetonitrile	Chloroform
Methanol	2-MeTHF	NMP
MEK	THF	DMF
1-Butanol	Xylenes	Pyridine
t-Butanol	DMSO	DMAc
	Acetic Acid	Dioxane
	Ethylene Glycol	Dimethoxyethane
		Benzene
		Carbon tetrachloride

Green Chem. **2008**, *10*, 31–36.

Water-free Condensers

- Reactions are often done in boiling solvents
- Condensers keep solvent volumes constant
- Metal-jacketed “Findensers” save water, eliminate flooding



Normal condenser

Water-free “Findenser” (Radleys)

Mobile Flammable Materials Freezer

- Chemicals and residential units don’t mix!
- A mobile freezer was acquired with Sust. CU & Green Labs funding; labs can safely defrost or have a replacement when a freezer breaks
- Encourages freezer cleanouts & proper chemical storage

https:
2014/ ... gerator-
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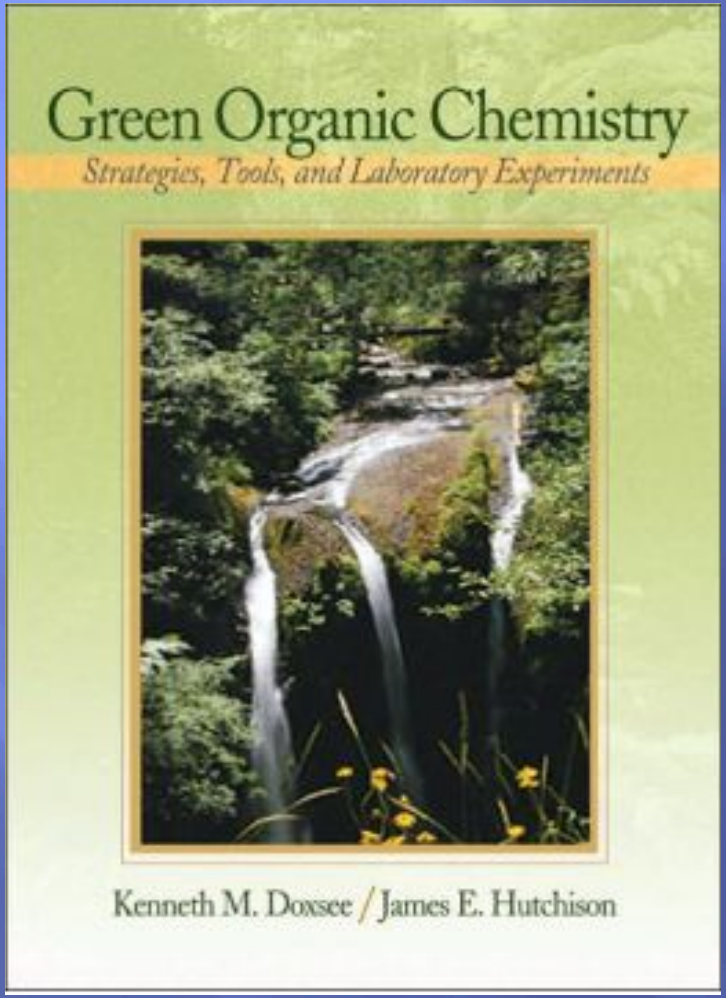
FY '14– '15 Green Chemistry Fund

- $5,000 fund to cover cost of materials for lab members to try their ideas
- Committee of grad students, EH&S & CU Green Labs to review requests
- Successes will be publically shared with campus
- Grow the green chemistry culture on campus and get labs involved in coming up with ideas
- Ideas that committee could also promote:
  - Replace EtBr with less toxic products for DNA viewing
  - Safer & greener alternatives to Piranha acid baths
  - Mercury free efforts

Green Chemistry Initiatives

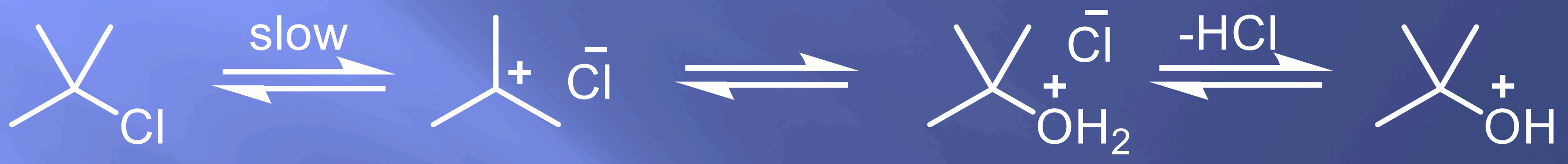


- 5 CU-Boulder Organic Chem teachings labs replaced with Green Chem alternatives per this book
- Impacts more than 800 students/year
- At Univ. of Oregon, only one third of Organic Chemistry teaching lab experiments require fume hoods

Goals of Green Chemistry

- Scaling down of reactions
- Replacement of hazardous procedures
- Substitution for less hazardous reagents
- Undergraduate education about hazards, acetone recycling, etc.
- A handful of reactions have been replaced and/or implemented
- Impacting up to 1000 students/year

Measuring solvent effects: kinetics of hydrolysis of tert-butyl chloride



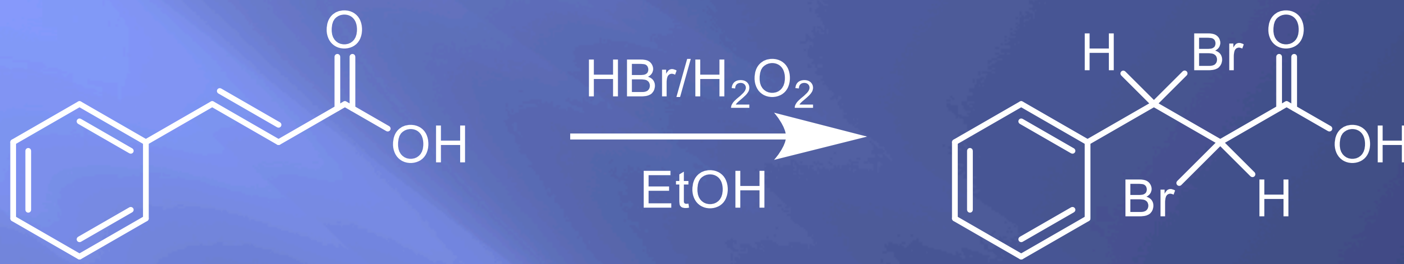
Previously:

- Replaces an old kinetics lab, which generated less volume of waste, but students used more hazardous reagents (KOH pellets, volatile alkylhalides)

Now:

- Milder reagents:
  - Uses recycled acetone and tap water as solvents
  - Prepared 0.04 M NaOH aqueous solution

A Greener Bromination of Stilbene



trans-Cinnamic acid

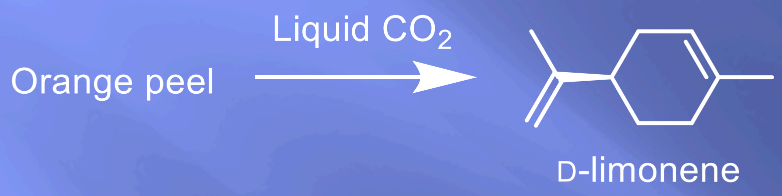
Previously:

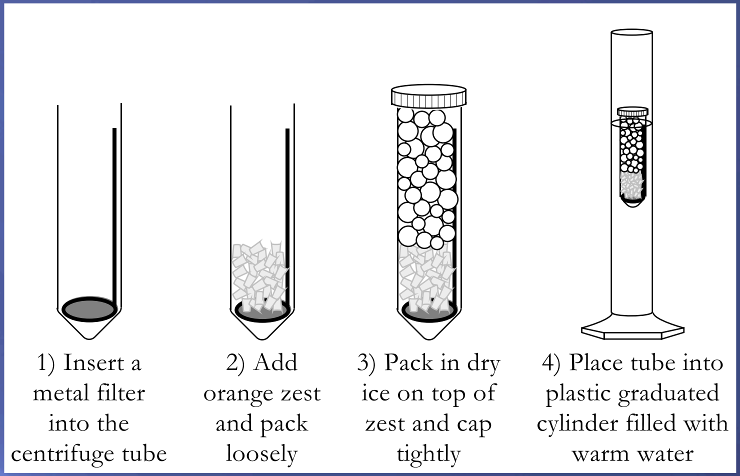
- Bromine solution, dichloromethane as solvent
- Large volumes of aq. sodium thiosulfate neutralized Br_2

Now:

- Br_2 generated in situ with H_2O_2 and HBr, ethanol used as solvent, and no aq. sodium thiosulfate needed

CO_2 Liquid Extraction of Limonene





Previously:

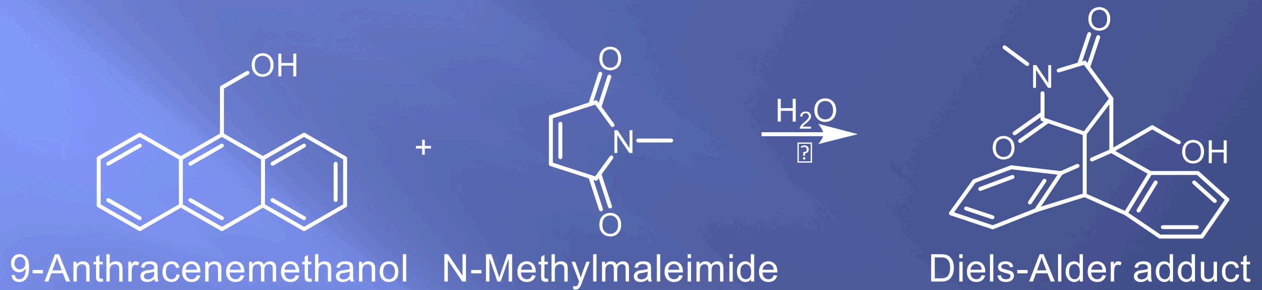
- Energy intensive steam distillation extraction procedure
- Required about 1 orange/student—high volume of discarded oranges

Now:

- Liquid CO_2 is more efficient, new digital polarimeter allows lower detection of limonene → ~1 orange/5 students!

McKenzie, L. C. et al., *Green Chem.* 2004, *6*, 355–358.

Green Diels-Alder



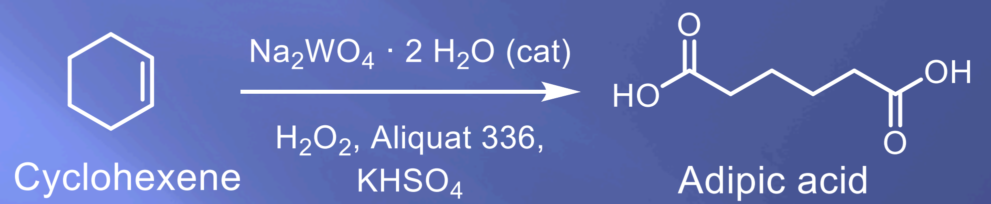
Previously:

- Precursor (cyclopentadiene) requires energy-intensive distillation before use and is volatile and noxious-smelling
- Large amounts of energy and solvents needed to purify product (and time – this lab always ran overtime)

Now:

- Solvent is water – no organic solvents used
- Product crystallizes automatically – no further purification needed

Green Oxidative Cleavage



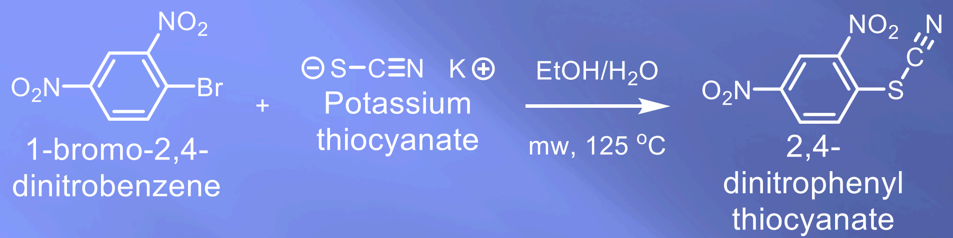
Previously:

- Traditional reaction could not be performed in teaching labs because it required either generation of ozone, or extremely toxic chromium- or manganese-based reagents

Now:

- Hydrogen peroxide used as oxidizer
- Tungsten used as catalyst
- Water used as solvent – students learn about phase transfer catalysts which allow reagent/catalyst to mix with water

Microwave-Assisted Chemistry



Previously:

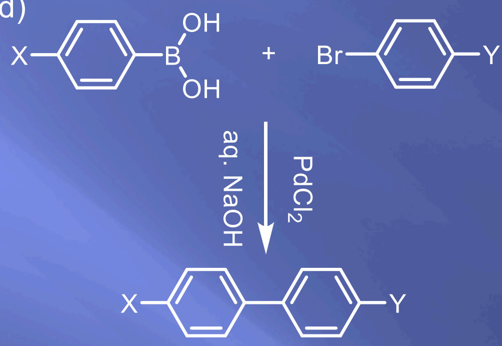
- Reaction needed week-long heating, large amounts of solvent, and large amounts of water run through condenser

Now:

- Microwave reactor allows reaction to proceed in 30 minutes with less energy input
- Green solvent – water and/or ethanol are good microwave absorbers
- Smaller reaction scale and less waste

Green Suzuki Coupling

X = H (phenylboronic acid)
X = OCH_3 (4-methoxy-phenylboronic acid)



Y = H (bromobenzene)
Y = $COCH_3$ (4'-bromoacetophenone)
Y = CH_3 (4-bromotoluene)
Y = OCH_3 (4-bromoanisole)
Y = F (1-bromo-4-fluorobenzene)

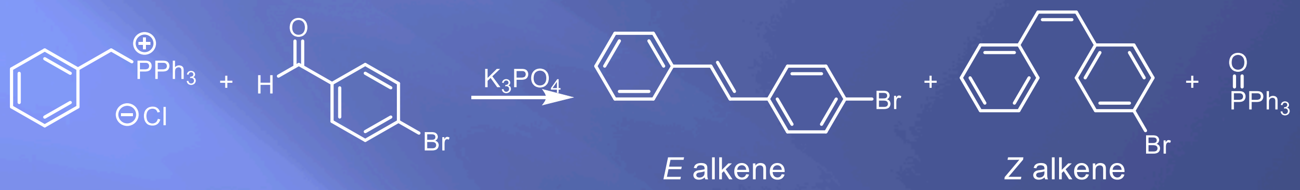
Previously:

- Traditional Suzuki catalyst is air-sensitive – requires use of nitrogen or argon atmosphere

Now:

- Palladium catalyst is still air-sensitive, but oxidizes slowly enough to perform reaction
- Aqueous solvent
- $PdCl_2$ commercially available as dilute solution – allows reaction to be easily performed on microscale, using less reagents

Solvent-Free Wittig Coupling



Previously:

- Mix two noxious-smelling, air-sensitive, toxic compounds with a flammable strong base

Now:

- Weigh out three inert solids and grind with mortar and pestle for 20 minutes, then mix with water and filter
- Product is better suited to teach students analysis of double bond isomers

Most Important: Changing Students' Perceptions of Chemistry

Previously:

- Student view of chemistry: no regard for environmental damage

Now:

- Green chemistry a specific goal of about one third of experiments currently in use
- Minimizing waste and maximizing efficiency are important goals, both in industry and in the lab

Future Goals:

- Phase out traditional organic solvents: hexane, dichloromethane
- Replace more old experiments with greener versions
- Put together videos explaining waste minimizatio cleaning glassware with minimum of solvent, how to avoid mixing waste streams, etc.

GREEN CHEMISTRY