Safety Starts with U

Paradigm Shift in Approach to Safety through Green Chemistry

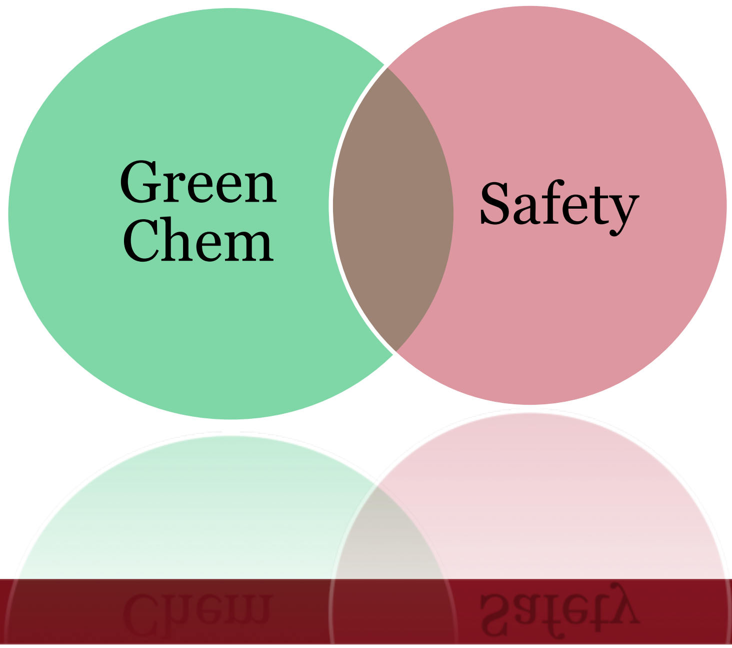
Jane Wissinger
University of Minnesota
June 13, 2019, 10:30 -10:50 AM, Lake, Audubon

23rd Annual Green Chemistry & Engineering Conference/9th International Conference on Green & Sustainable Chemistry

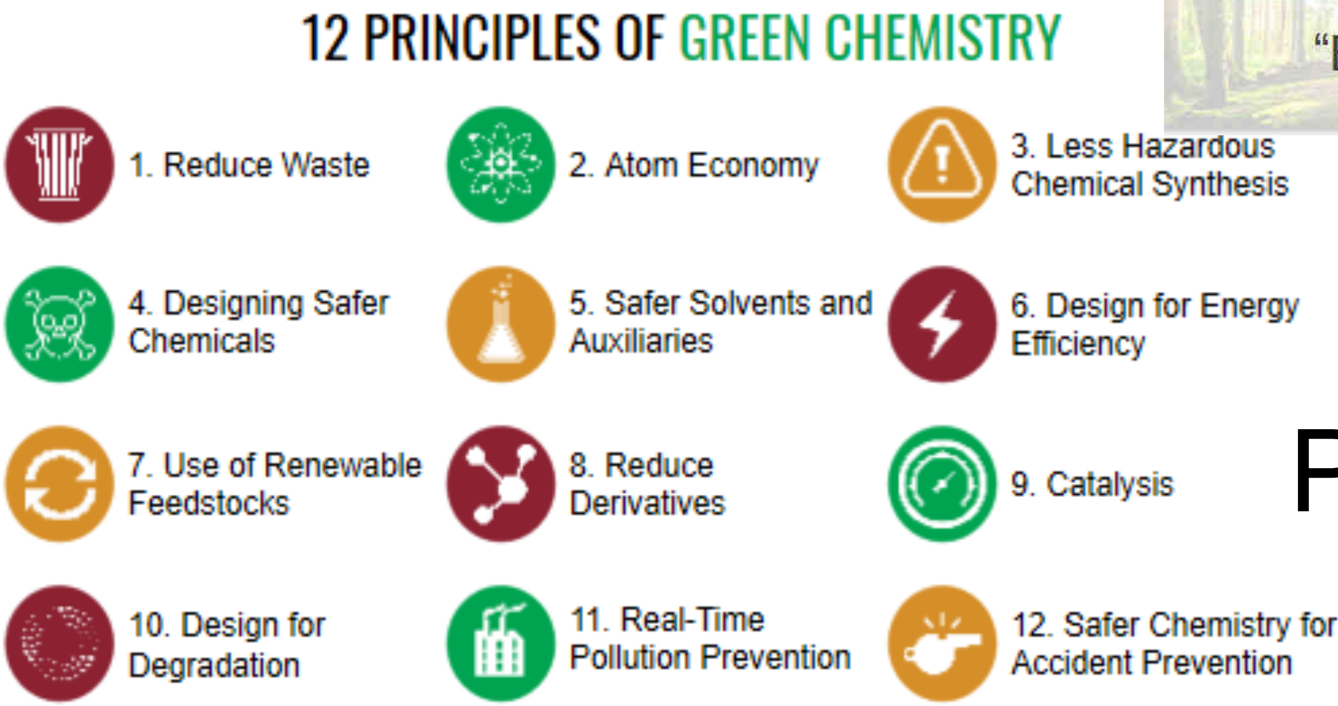
Hyatt Regency, Reston, VA

Overview

- Intersecting Goals of Green Chemistry & Safety
- Green Chemistry Principles & RAMP Education Model
  - Assessing Risk
- Greener/Safer Teaching Lab
- Green Chemistry/Safety Collaborations



Green Chemistry



Prevention

Chemical Safety

Safety in the Chemistry Enterprise

“the practice of chemistry must be done safely so as to minimize adverse impacts on human health and or the environment”

Protect

Covered in training courses by EHS required for compliant lab work

https://www.acs.org/content/acs/en/policy/publicpolicies/science-policy/safety-in-the-chemistry-enterprise.html
https://www.acs.org/content/dam/acsorg/about/strategicplan/acs-strategicplan-infographic-2019.pdf

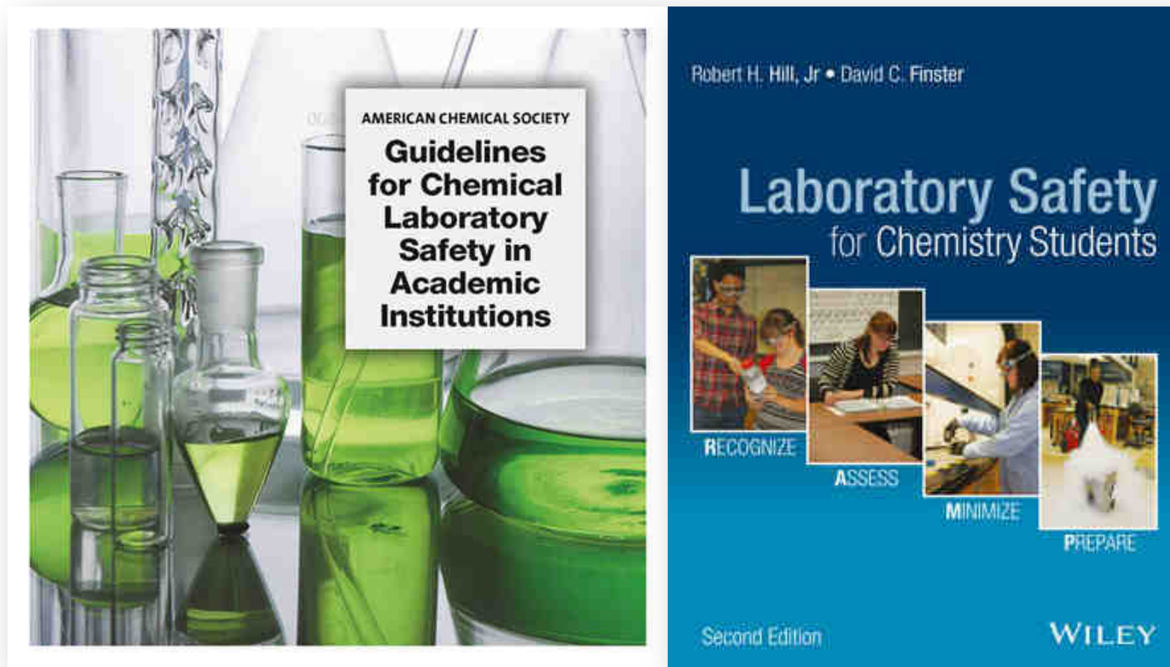
ACS promotes R-A-M-P student learning tool

Recognize the hazards

Assess the Risks of Hazards

Minimize the Risk of Hazards

Prepare for Emergencies from Uncontrolled Hazards



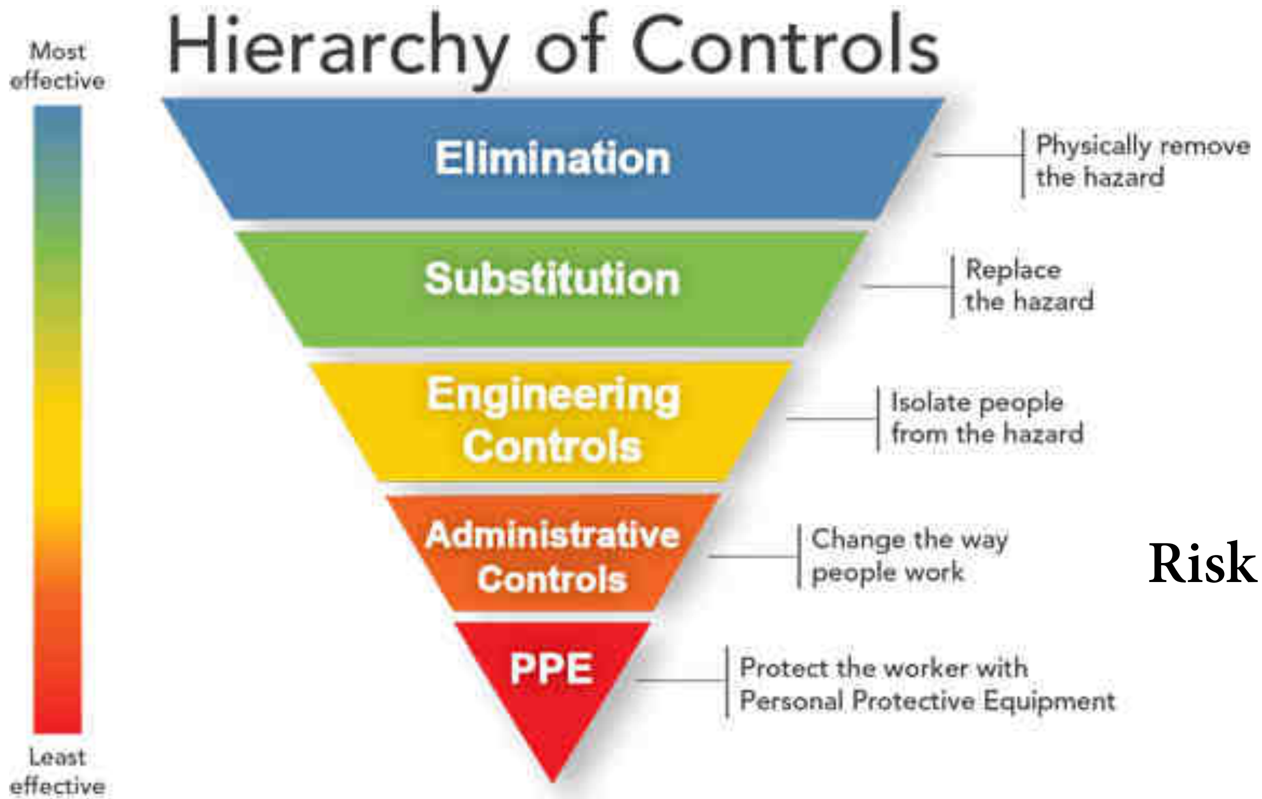
Paradigm shift from compliance focus to assessment focus

Complementary

Green Principles

RAMP

National Institute for Occupational Safety and Health NIOSH (Hazards Control)

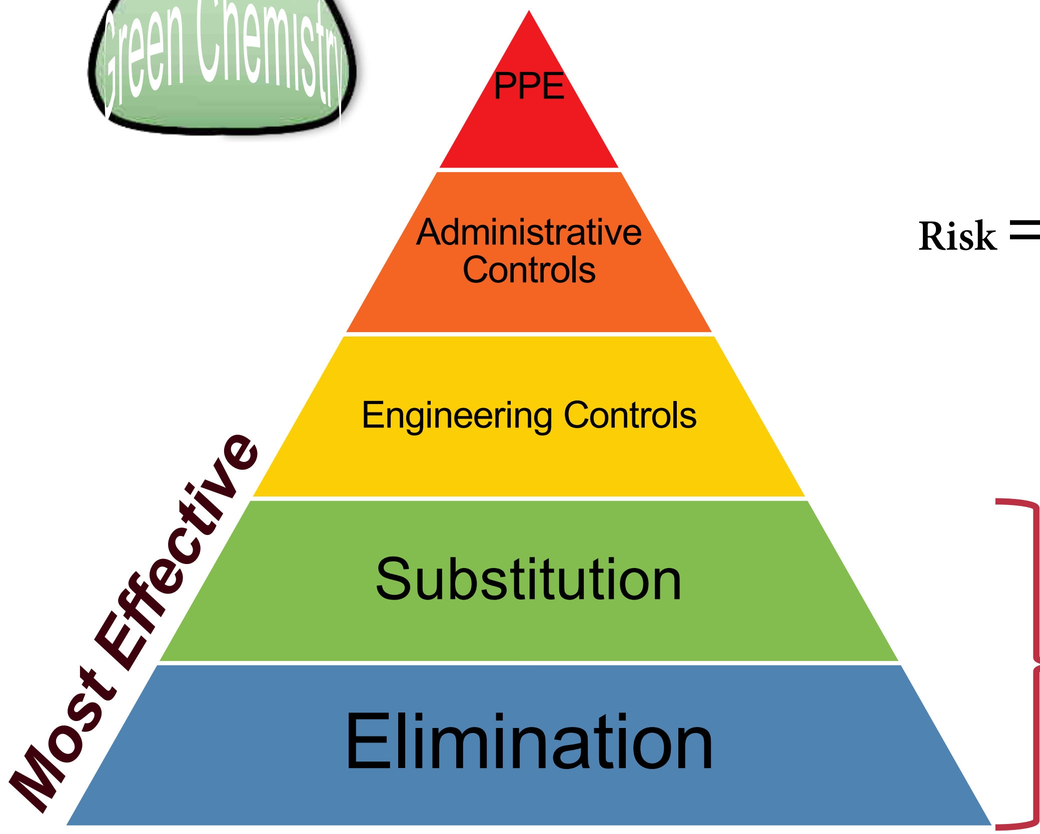


GREEN CHEMISTRY

$$\text{Risk} = f\,(\text{exposure, hazard})$$

GC strategy is to minimize risk by reducing the <u>HAZARD</u>

$$\text{Risk} = f\,(\textbf{exposure}, \text{ hazard})$$

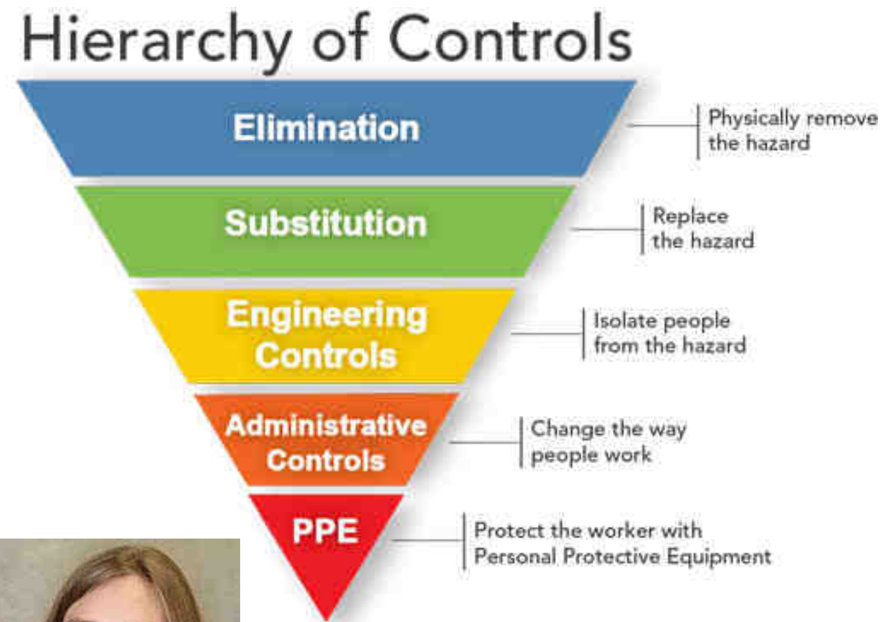


GREEN CHEMISTRY

Caution – Singular focus on a green principle can have unintended consequence for safety

Ventilation

Unintended consequences - reducing **necessary** control



Anna Sitek – U of MN Research Safety Professional

Better Together

Paradigm shift – *from rules to assessment*

Collaboration helps identify unconscious incompetency in safety understanding

1. Unconscious Incompetence **“Don’t know, what you don’t know”**	**2. Conscious Incompetence** Learning “know, you don’t”
3. Conscious Competence Proficient	**4. Unconscious Competence** **“Could do it in my sleep”**

- Collaborations
- Systems Thinking
- Safety Culture
  - Peer evaluation

Conscious Competency Model
https://en.wikipedia.org/wiki/Four_stages_of_competence
Broadwell, Martin M. (20 February 1969). "Teaching for learning (XVI)". *wordsfitlyspoken.org*. The Gospel Guardian. Retrieved 11 May 2018.

Ramp Recognize

Chemical Safety

- SDS – similar starting places (GHS)
- Green Chemistry Metrics (Analyze)
  - Compare processes for design
  - Type of reaction
  - Atom economy (intrinsic/inherent)
  - Focus NOT just on yield of desired products, but possible by-products and their hazards/waste handling
  - Energy and water use considerations

Physical & Reaction Hazards

rAmp Assess the risk

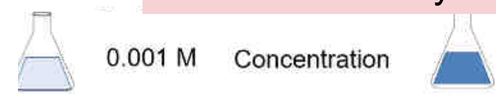
Risk = Function (Exposure, Severity of hazard)

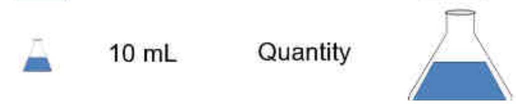
Routes of Exposure to the environment

Routes of Exposure to people

Green Chemistry provides understanding how to change hazard severity

What the severity is


0.001 M Concentration 1 M


10 mL Quantity 10 L

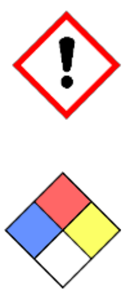

Duration

Environmental Conditions

Compatibility

Solvent	ABS	LDPE	HDPE	PC	PMP	PP	PS	PTFE
Acetaldehyde	D	C	B	C	C	C	D	A
Acetic Anhydride	C	D	D	D	B	B	D	A
Acetone	D	C	C	D	A	A	D	A
Acid, Hydroflouric	C	A	A	D	A	B	D	A
Acid, Trifluoroacetic	D	D	C	D	D	D	D	A
Acid, Acetic Dilute 50%	A	A	A	B	A	A	B	A

A	No Effect, excellent compatibility
B	Minor Effect, good compatibility
C	Moderate Effect, fair compatibility
D	Severe Effect, not recommended
-	No data available



GHS	1- extremely hazardous	2- highly hazardous	3- Hazardous	4- harmful	5- may be harmful
NFPA	4- extremely hazardous	3- highly hazardous	2- hazardous	1- harmful	0- no risk

rAmp Assess the risk

New Resources for Learning Chemical Toxicology Promoted by Green Chemists

Chemical Safety

Teaching chemists appropriate level of toxicology

– Better understanding promotes safer design of processes and products
– Relationship of MW to toxicity
– Relationship of $LogK_{ow}$ to toxicity
– ADME (Absorption, Distribution, Metabolism, Excretion)

https://modrn.yale.edu/

https://modrn.yale.edu/education

rAmp Assess the risk

“Even if the synthesis of an organometal poly azido detonated the first six times the chemist did it, the published paper will very likely not mention it.”
Langerman https://doi.org/10.1016/j.jchas.2015.04.005

WARNING! Relevant hazards are NOT included in Published literature.

- Only recently have some publications required safety to be included
- Even in journals where required, very few safety references are made.
- **Essential to do your own Hazard Assessment!**

What has been done in the past ≠ best (or even safe) practice

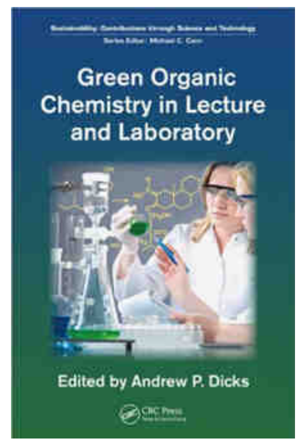
If you haven’t considered a green chemistry substitution, you probably haven’t done an assessment and are relying on a false assumption of safety - AS

Resources for Elimination or Substitution

- Increasing amount of literature examples/resources
- Solvent replacements
- Solventless reaction examples

Ball Milling

ACS Sustainable Chemistry & Engineering



beyondbenign
green chemistry education

Solvent Selection Guides

Preferred

- Water
- Acetone
- Ethanol
- 2-Propanol
- 1-Propanol
- Ethyl acetate
- Isopropyl acetate
- Methanol
- Methyl ethyl ketone
- 1-Butanol
- *t*-Butanol

Usable

- Cyclohexane
- Heptane
- Toluene
- Methylcyclohexane
- Methyl *t*-butyl ether
- Isooctane
- Acetonitrile
- 2-MethylTHF
- Tetrahydrofuran
- Xylenes
- Dimethyl sulfoxide
- Acetic acid
- Ethylene glycol

Undesirable

- Pentane
- Hexane(s)
- Di-isopropyl ether
- Diethyl ether
- Dichloromethane
- Dichloroethane
- Chloroform
- Dimethyl formamide
- *N*-Methylpyrrolidinone
- Pyridine
- Dimethyl acetate
- Dioxane
- Dimethoxyethane
- Benzene
- Carbon tetrachloride

Fig. 1 Pfizer solvent selection guide for medicinal chemistry.

ACS Green Chemistry Institute®
Pharmaceutical Roundtable

Scoring Information				
Safety	Health	Env (Air)	Env (Water)	Env (Waste)
3	6	6	3	6
3	6	6	2	7
2	6	5	4	7
		6	6	10
2	5	6	4	6
3	5	5	5	3
4	4	6	2	6

GSK Solvent Selection Guide 2009

Classification	Solvent	CAS number	Melting point °C	Boiling point °C	Waste recycling, incineration, VOC and biotreatment issues	Environmental Impact fate and effects on the environment	Health acute and chronic effects on human health and exposure potential	Flammability & Explosion storage and handling	Reactivity/Stability factors affecting the stability of the solvent	Life Cycle Score Environmental impacts to produce the solvent	Legislation Flag alerts regulatory restrictions
Greenest	Water	7732-18-5	0	100	4	10	10	10	10	10	
Alcohols	1-Butanol	71-36-3	-89	118	5	7	5	8	9	5	
	2-Butanol	78-92-2	-115	100	4	6	8	7	9	6	
	Ethanol/IMS	64-17-5	-114	78	3	8	9	6	9	8	
	t-Butanol	75-65-0	25	82	3	9	6	6	10	6	
	Methanol	67-56-1	-98	65	4	9	5	5	10	8	
	2-Propanol	67-63-0	-88	82	3	9	8	6	8	4	
	1-Propanol	71-23-8	-127	97	4	7	5	7	10	7	
	2-Methoxyethanol	109-86-4	-85	124	3	8	2	7	6	7	
Ester	t-Butyl acetate	540-88-5	-78	95	6	9	8	6	10	8	
	Isopropyl acetate	108-21-4	-73	89	6	7	7	6	9	7	
	Propyl acetate	109-60-4	-92	102	5	7	8	6	10	4	
	Dimethyl carbonate	616-38-6	-1	91	4	8	7	6	10	8	
	Ethyl acetate	141-78-6	-84	77	4	8	8	4	9	6	
	Methyl acetate	79-20-9	-98	57	3	9	7	4	9	7	
Ketone	Methylisobutyl ketone	108-10-1	-84	117	6	6	6	7	8	3	
	Acetone	67-64-1	-95	56	3	9	8	4	9	7	
	Methylethyl ketone	78-93-3	-87	80	3	7	8	4	8	3	
Organic Acids	Propionic acid	79-09-4	-21	141	4	8	6	8	8	7	
	Acetic acid (glacial)	64-19-7	17	118	4	8	6	8	7	8	
Aromatics	p-Xylene	106-42-3	-13	138	7	2	6	5	10	7	
	Toluene	108-88-3	-95	111	6	3	4	4	10	7	
	Benzene	71-43-2	6	80	5	6	1	3	10	7	
Hydrocarbons	Isooctane	540-84-1	-107	99	6	4	8	3	10	7	
	Cyclohexane	110-82-7	7	81	5	5	7	3	10	7	
	Heptane	142-82-5	-91	98	6	3	8	3	10	7	
	2-Methylpentane	107-83-5	-153	60	5	4	7	3	10	7	
	Hexane	110-54-3	-95	69	5	3	4	3	10	7	
	Petroleum spirit	8032-32-4	-73	55	6	2	3	3	10	7	
Ethers	t-Butyl methyl ether	1634-04-4	-109	55	4	5	5	3	8	8	
	Cyclopentyl methyl ether	5614-37-9	-140	106	6	4	4	6	8	4	
	2-Methyl THF	96-47-9	-137	78	4	5	4	3	6	4	
	Diethyl ether	60-29-7	-116	35	4	4	5	2	4	6	
	Bis(2-methoxyethyl) ether	111-96-6	-68	162	4	5	3	8	4	6	
	1,4-Dioxane	123-91-1	12	102	3	4	4	4	5	6	
	Tetrahydrofuran	109-99-9	-108	65	3	5	6	3	4	4	
	1,2-Dimethoxyethane	110-71-4	-58	85	4	5	3	4	4	7	
	Diisopropyl ether	108-20-3	-86	68	4	3	8	1	1	8	
Dipolar aprotics	Dimethyl sulfoxide	67-68-5	18	189	6	5	7	8	3	6	
	Dimethyl formamide	68-12-2	-61	153	4	6	3	8	8	7	
	N-Methylformamide	123-39-7	-4	200	4	6	3	10	10	7	
	N-Methyl pyrrolidone	872-50-4	-24	202	5	6	3	8	8	4	
	Dimethyl acetamide	127-19-5	-20	165	5	6	3	10	8	3	
	Acetonitrile	75-05-8	-45	82	3	6	6	6	10	3	
Chlorinated	Carbon tetrachloride	56-23-5	-23	77	4	5	3	4	10	7	
	Dichloromethane	75-09-2	-95	40	3	6	4	8	9	7	
	Chloroform	67-66-3	-64	61	3	6	3	8	9	6	
	1,2-Dichloroethane	107-06-2	-35	84	4	4	3	8	10	7	

Legislation Flag	
(yellow)	Substitution recommended - There are no current restrictions but future regulatory restrictions may apply
(orange)	Substitution recommended - existing regulatory restrictions apply
(red)	Must be substituted - A regulatory ban applies

GSK SSG-MC-02 September 2010

GlaxoSmithKline

ramP Prepare for Emergencies & Protect Environment

Sustainable practices help prepare for problems

- Vacuum pump vs water aspirator – steady vacuum, protect sink
- Recirculating & water free condensers – prevent floods & water waste
- Inventory accuracy – avoid duplicates, monitor stability
- Housekeeping – can find & access materials; checking reuseable materials for integrity
- Unplugging equipment – unexpected heating

Green Organic Chemistry Laboratory Course

- **A green approach**

  - Modern
  - Greener Solvents (water, ethyl acetate, alcohols)
    - Reduce exposure
    - Reduced halogenated/heavy metal waste
  - Greener Reactions
    - Less potential for accidents
    - More variety (polymer-supported rxns, solventless)
    - New techniques

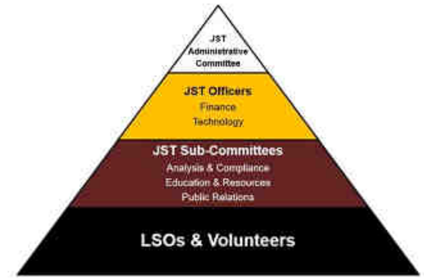
- **Reduced/Safer Waste**
  - Video - how to wash glassware
    Track waste containers per semester
    0.92 L down to 0.56 L per student

  - Less Concern for Hazardous Waste
    Example: strong oxidizers in organic waste
    Emphasis on not overfilling waste containers

Incorporation into a Safety Culture

Safety Starts with U

University of Minnesota



Joint Safety Team Organization

JST is compiled of Lab Safety Officers (LSOs) from each research group (~ 80 people) as well as volunteer undergraduates, graduates, and postdocs.

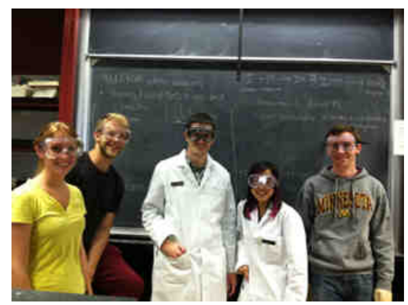
GC Initiatives with Joint Safety Team

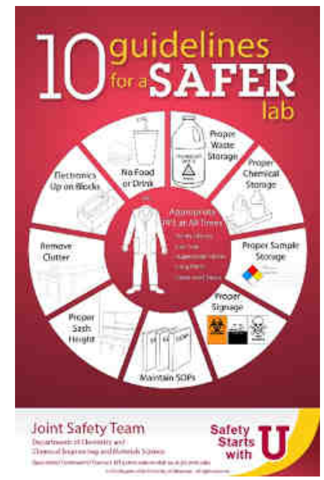
- **Provide substitution/elimination resources**
- Poster/stall wall moments
- Incorporation green chemistry into safety training
- Add safety moments with green chemistry
- Labs keep track of hazardous waste and set reduction goals
- Collaborate with stockroom to stock greener solvents

Safety Starts with U

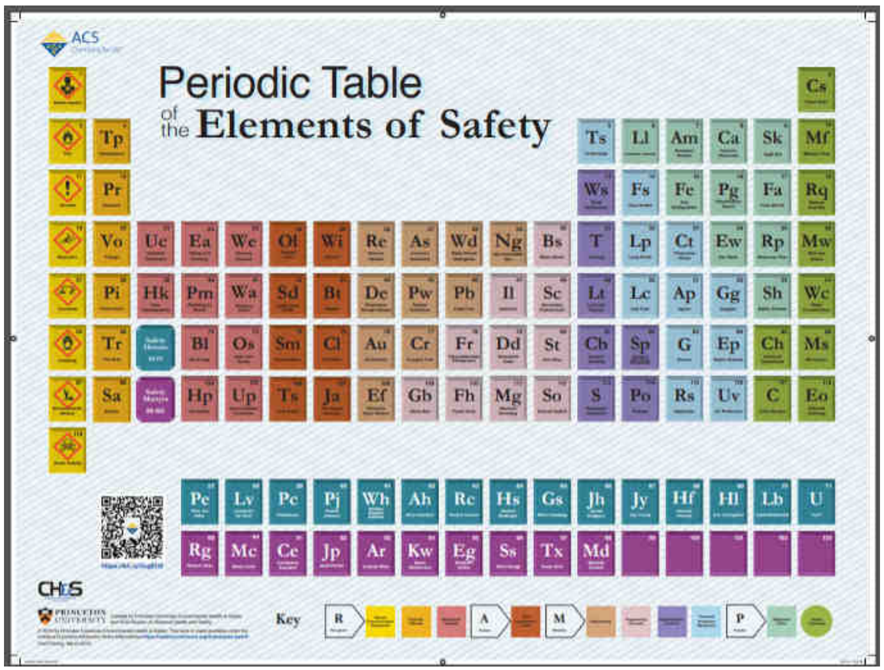
JST Website

Green solvent apps





Green Chemistry part of Elements of Safety



85 Ch — **Chemical Substitutes:** Substitute safer materials for polluting or toxic substances whenever possible.

117 C — **Cold Storage:** Updating refrigerators, cleaning door seals and filters, disposing of unneeded materials and consolidation of chemicals and reagents are all good ways to reduce energy costs.

2 Cs — **Close Sash:** Close the sash on a fume hood when not in use to reduce electricity consumption in the lab.

10 Mf — **Mercury Free:** Eliminate the use of mercury in experiments whenever possible to avoid the need to dispose of this hazardous metal.

18 Rq — **Reduce Quantity:** Reduce the amount of materials and resources used when possible.

36 Mw — **Minimize Waste:** Find alternatives to disposal such as sharing, redistribution and recycling.

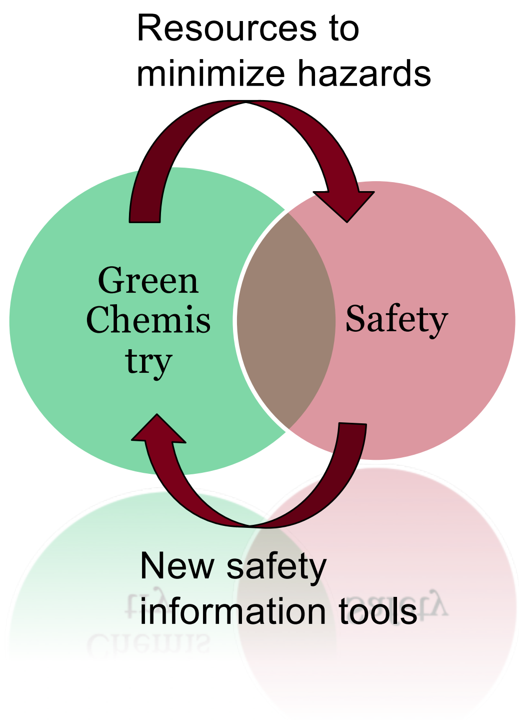
54 Wc — **Water Conservation:** Conserve water by using flow-reducing valves, reducing rinse cycles and running dishwashers only when they are full.

86 Ms — **Microscale:** Scaling down experiments saves time and resources, cuts down on storage needs and promotes safety in the lab.

118 Eo — **Efficient Ordering:** Utilize good inventory practices to reduce the amount of materials purchased and stored.

Conclusion

- Green Chemistry Goals and Safety Goals are synergistic
- EHS & faculty/instructor collaborations on green chemistry & safety training effective
- **Mindset** of utilizing green chemistry when possible will **enhance** safety of chemists and the environment



Journal of Chemical Education Call for Papers—Special Issue on Chemical Safety Education: Methods, Culture, and Green Chemistry

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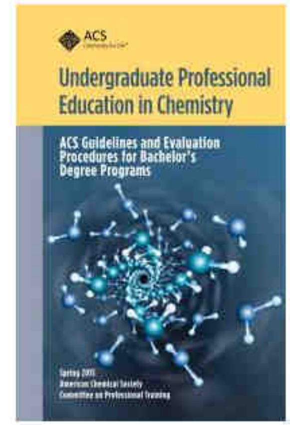
The editors welcome papers on the following topics, and any related topics that advance chemical safety education.

- **Teaching safety:** Methods of teaching chemical safety; undergraduate and graduate courses in chemical safety; safety training for primary and secondary school teachers; TA training; faculty safety training; safety videos
- **Hazard assessment and risk minimization:** Chemical safety information; integrating RAMP paradigm into chemistry education; using the ACS hazard analysis toolkit (checklist, control banding, standard operating procedure, job hazard analysis, what-if analyses); use of green alternative solvent and reagent guides
- **Safety benefits of green chemistry:** Connecting green chemistry to the RAMP paradigm; using green metrics to assess risk; selecting benign solvents and reagents; minimizing waste production and handling through use of catalysts and avoiding derivatizations and separations; strategic design of new chemicals with minimal human and environmental toxicity; choosing processes inherently safer for accident prevention
- **Safety resources:** Resources from the ACS, ACS Green Chemistry Institute (GCI), DCHAS, Corporation Associates, Lab Safety Institute, NSTA, NFPA, CSB; using and interpreting the SDS
- **Industrial safety:** Safety training; industrial expectations for the safety background of newly hired chemists
- **Engineered safety:** Fume hoods; distillation safety; radiation safety (X-ray, laser, RF, UV, nuclear, etc.); biosafety; pyrophorics; vacuum safety
- **Academic environments:** Laboratory size and student load; chemical preparation and storage areas; teaching and research safety equipment; preservice teacher training; safe demonstrations
- **Accident analysis:** CSB studies; organolithium accidents; root cause analysis
- **Building cultures of safety:** Academic, including student-lead programs; government; industrial settings
- **Informal education:** Outreach; household chemicals

Safety Starts with U

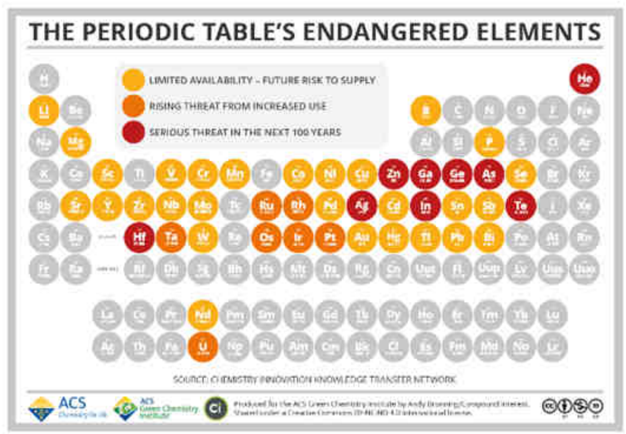
Questions?

CPT Supplement on Green Chemistry



- What's in this supplement?
  - ***Making the case for green and sustainable chemistry.***
    - SAFER chemistry departments
    - Preparing students for future careers
    - Modern and innovative
    - Chemical enterprise contributions to sustainability

- Practical Examples – Like Safety (cross disciplinary)
  - General Chemistry
  - Analytical Chemistry
  - Biochemistry
  - Inorganic Chemistry
  - Organic Chemistry
  - Physical Chemistry



Safety in the Chemistry Enterprise Policy Statement (2016-2019)

- Chemical management and regulatory policy should foster technological innovation and a globally competitive US chemical industry. Advancing research and **applying appropriate green and sustainable principles will lead to economically viable technical innovations.** To this end, ACS supports the government implementation of:

- An expedited, rigorous treatment of regulatory applications for **inherently safer chemical products and processes.** The government should work with industry, academia, scientific organizations, public interest groups, and other stakeholders to develop guidelines for use in such a regulatory process.