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#### Nanomaterial Design Guided by the Principles of Green Chemistry

#### Thursday, May 18 @ 2-3pm ET



How can green chemistry be applied to nanotechnology to achieve the high performance needed for advanced applications while preventing or reducing health and environmental impacts? Join James Hutchison from the University of Oregon as he discusses the foundations for greener nanotechnology and presents a case study that uses nanomaterial product innovation guided by green chemistry.



#### What You Will Learn

- The opportunity to achieve a net environmental benefit by bringing together green chemistry with nanoscience
- The role that green chemistry plays in designing high performance nanomaterials and efficient nanomaterial production
- How green chemistry and nanoscience can be used together to develop innovative new products with environmental benefits

http://bit.ly/GreenNano





#### **Experts**



James Hutchison University of Oregon



Howard University

Joe Fortunak

#### **Co-Produced With**



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# 2017 DCHAS Workshops

The division is dedicated to supporting the efforts of chemical manufacturers, industrial and academic researchers, and science teachers at all levels to work for a safe and healthful work environment. Through our technical symposia, the Division's Journal, the Journal of Chemical Health and Safety, our workshops and our DCHAS-L listserv, we provide a forum for scholarly health and safety research, advice and counsel from an experienced group, and support for health and safety efforts in industry and academia.

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Thursday, May 25, 2017



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# **Anti-Infectives:** Rational Approaches to the Design and Optimization

Co-produced with the ACS Division of Medicinal Chemistry and the AAPS
Jason Sello, Associate Professor of Chemistry, Brown University

**Courtney Aldrich**, Associate Professor, Department of Medicinal Chemistry, University of Minnesota and Editor-in-Chief of *ACS Infectious Diseases* 

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**Creating a 21st Century Chemical Research Laboratory:** Hazard Assessments and Fundamentals



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This ACS Webinar is co-produced by the ACS Division of Chemical Health and Safety and the ACS Green Chemistry Institute

## **CREATING A 21ST CENTURY CHEMICAL RESEARCH LABORATORY:** HAZARD ASSESSMENTS AND FUNDAMENTALS



Dr. Kendra Leahy Denlinger University of Cincinnati

Ralph Stuart, CIH, CCHO Chemical Hygiene Officer, Keene State College Secretary, Division of Chemical Health and Safety, American Chemical Society



Keene state college

MAY 11, 2017

# SAFETY WITHIN THE ACS VISION





### **MOVING LAB SAFETY INTO THE 21ST CENTURY**

### Lab Safety involves both Technical and Cultural Skills



### **TECHNICAL CHEMICAL SAFETY RESOURCES**



## **RESEARCH RISK ASSESSMENT RESOURCES**

#### National Research Council, 2011









# **OTHER KEY TECHNICAL TOOLS**

#### **National Library of Medicine's Pubchem**

Laboratory Chemical Safety Summaries (2015)

- Safety information on 103,000 chemicals
- Includes SDS-style information as well as specific reaction information between chemicals



### Pistoia Alliance Chemical Safety Library (2017)

- Information on specific lab scale chemical incidents
- Access is free upon registrantion and reporting of incidents is encouraged.



# **CULTURAL LAB SAFETY RESOURCES**



### **KEY RESEARCH SAFETY CULTURE RESOURCES**

National Research Council, 2014	ACS, 2016
	ACS Central Science Ingredients for a Positive Safety Culture
BAFE SCIENCE Drotten a Calture of Safety in Academic Chemical Research	Home > Volume 94 Issue 48 > ACS journals enact new safety policy Volume 94 Issue 48   p. 7   News of The Week Issue Date: December 5, 2018   Web Date: December 1, 2018 ACS journals enact new safety policy Authors to be required to address novel or significant hazards By Jyllan Kemsley



### Which hazard MOST concerns you?

- Chemicals of known reactivity
- · Chemicals of known toxicity
- · Environmentally hazardous chemicals
- · Chemicals of unknown toxicity

# A LESSON IN LAB SAFETY



1319	Causes serious eye imitation.
H335	May cause respiratory irritation.
H361	Suspected of damaging fertility or the unborn child.
H371	May cause damage to organs (Nervous system) if swallowed.
H372	Causes damage to organs (Kidney) through prolonged or repeated exposure if swallowed.
H410	Very toxic to aquatic life with long lasting effects.



https://ehs.unl.edu/sop/s-health\_hazards\_haz\_assessment\_risk\_min.pdf

# **A LESSON IN LAB SAFETY**

Mack Lab Safety Form for Ordering Toxic Chemicals	
It is mandatory to fill out this form if the chemical you are ordering is labeled with any of the following HCS Pictograms:	
	SH
Chemical name:	~
Chemical structure:	
Using the MSDS or SDS for this chemical, list ALL of the potential human health hazards, including routes of exposure (ex. Inhalation, sidn contact, ingestion, etc.).	$LC_{50} \leq 2.0 \text{ mg/L}$
Provide a detailed explanation of why this chemical is essential to your research.	
For each of the human health hazards you listed above, explain them in more detail here using the table below, adding more rows if necessary. Some of this can be obtained from the MSDS or SDS, but some will need to be obtained from other sources.	
Hazard LD <sub>10</sub> or LC <sub>30</sub> First Aid Symptoms of Pathophysiology Statement Measures exposure (what does it affect in your body?)	
 What alternatives to this chemical are available? Why can these not be substituted for this chemical?	
Now that the possible consequences of using this chemical have been described, please explain how the benefits to your research outweigh the potential costs to our health.	23



Safety in the laboratory requires a full team effort to be successful. When everyone in the laboratory understands how to identify hazards, assess risk, and select the appropriate control measures to eliminate a hazard or minimize risk, accidents, injuries and near misses can be reduced.



https://www.acs.org/hazardassessment

# HAZARD VS. RISK

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### Risk = hazard x exposure







Alder, C. et. al. "Updating and further expanding GSK's solvent sustainability guide." *Green Chemistry*, **2016**, *4*, 1166-1169.

## **HIGH-SPEED BALL MILLING**





# **BALL MILLING VS. SOLUTION**



# **CHROMATOGRAPHY**

Table 5.8 Column Chromatography Materials				
Stationary Phase		Moving Phase		
Alumina /	Increasing	Water /	Increasing	
Silicic acid	adsorption	Methanol	solvation	
Magnesium sulfate	of polar	Ethanol	of polar	
Cellulose paper	materials	Acetone	materials	
		Ethyl acetate		
		Diethyl ether		
		Methylene chloride		
		Cyclohexane		
		Pentane		



Mayo, Dana W.; Pike, Ronald M.; Forbes, David C. *Microscale Organic Laboratory*. United States: John Wiley & Sons, Inc., 2011. Print.

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# **FUNCTIONALIZED POLYMER RESINS**





# WHAT SHOULD BE ATTACHED?

### Design the reaction so that:

- A product is attached to the polymer
- A **byproduct** is attached to the polymer
- A catalyst is attached to the polymer





Polystyrene 1-2% Cross-linked with divinylbenzene

## WITTIG REACTION

- 1950's
  Nobel Prize awarded in 1970's
- Harmful organic solvents
- Very strong bases (n-BuLi)





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## WITTIG REACTION WITH POLYMER RESIN





# Have you developed Green Chemistry alternatives for specific reactions in your lab work?

- Yes, we have developed a full set of GC alternatives
- Yes, we have developed some GC alternatives
- Yes, we have developed a few GC alternatives
- No, we have not developed any GC alternatives yet



# **DETERMINE THE SCOPE**

#### **Collect Appropriate Background Information**

The analysis team will need appropriate background information, including:

- Equipment diagrams
- A list describing common hazards associated with chemicals and gases
- A list of the equipment's chemical and gas compositions, operating pressures, flow rates, run times, and other applicable parameters
- Potential health and physical hazards of equipment (e.g., ionizing or nonionizing radiation, high temperature, high voltage, or mechanical pinch points)
- · Equipment safety features (e.g., interlocks)
- Physical access to equipment, as necessary/possible

Safety Data Sheets can include a lot of this information.





#### Assemble Your Team

Everyone should be involved in hazard assessment, regardless of experience level or title in the lab.

*Everyone* is responsible for familiarizing themselves with appropriate controls for the hazards discovered in the lab.

*Everyone* is responsible for participating in hazard analyses (checklists, Job Hazard Analysis, and What-if Analysis) and the updating of the lab's Standard Operating Procedures. This is also a good time to review accidents, incidents, and near misses and collectively brainstorm ways to prevent these events in the future.

More experienced members of the team should lead risk assessment activities and assign risk ratings to the materials and processes in your lab.

Learn about the roles and responsibilities of various people in the lab.



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# **CONDUCTING A HAZARD ASSESSMENT**



### <u>Identify hazards</u> → Analyze risks → Select controls

Ways to Conduct a Hazard Assessment					
Hazard Ass	essment	Fundamentals	Ways to Conduct As	sessments	
Vhat-if Analysis	Job Hazard Analysis	Checklists	Standard Operating Procedures	Control Banding	
	1				
				38	

### Identify hazards $\rightarrow$ <u>Analyze risks</u> $\rightarrow$ Select controls

# Calculate Risks Using Probability of Occurrence and Severity of Consequences Scaling

Many risk assessments use "probability of occurrence" and "severity of consequences" scales to rate risks associated with laboratory experiments. They are comprehensive assessment tools and provide greater differentiation of risks based on actual laboratory operations.

Using this kind of scaling, laboratory hazard risk rating is calculated as follows:

Risk Rating (RR) = Probability of Occurrence (OV) x Severity of Consequences Value (CV)

As the formula indicates, the higher the assessed probability of occurrence and severity of consequences, the greater the risk rating will be.



### Identify hazards $\rightarrow$ <u>Analyze risks</u> $\rightarrow$ Select controls

Probability of Occurrence with Standard Linear Scaling

Occurrence Value (OV)		Probability of Occurrence	
ting	Value	Percent	Description
t Present	0	0%	Item/operation is not present in laboratory.
re	1	1-10%	Rare
ssible	2	10-50%	Possible
cely	3	50-90%	Likely
most Certain to Certain	4	90-100%	Almost Certain to Certain

Severity of Consequences, Weighted Value Scale

Ra No Ra Po Li

Consequ Value (	ence CV)	Impact to				
Rating	Value	Personnel Safety	Resources	Work Performance	Property Damage	Reputation
No Risk	1	No injuries	No impact	No delays	Minor	No impact
Minor	5	Minor injuries	Moderate impact	Modest delays	Moderate	Potential damage
Moderate	10	Moderate to life impacting injuries	Additional resources required	Significant delays	Substantial	Damaged
High	20	Life threatening injuries from single exposure	Institutional resources required	Major operational disruptions	Severe	Loss of confidence

high probability x no consequences = 4 low probability x life threatening consequences = 20



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		Job Haz	ard Analysis		
Job Location: <u>Rieveschl</u> Ha	all, UC La	aboratory (	iroup: Mack Date	e: 03/14/2017	
Activity or Job	Run Wittig reaction				
Completed By	Kendra				
Equipment and Chemicals Required	pipette, rubb carbonate, be	er pipette t enzaldehyd	, o-ring, stainless steel t oulb, metal spatula, PS-F e	all, balance, ball mill, glass PPh <sub>2</sub> , benzyl bromide, cesium	
Work Steps and Tasks Describe the tasks or steps involved in the work in the order performed	Hazards Iden each Task/St	tified for ep	Risk Level Risk <u>Nomogram</u> .can be used (see APPENDIX B)	Control/Safe Work Procedures for each Task/Step Controls to be implemented	
. ,	Combustib	le liquid	1 x 5 = 5	Do not handle near open flame or sources of ignition	
Weigh out benzyl	Causes skin	irritation	1 x 5 = 5	Use PPE; discard contaminated gloves immediately; wash hand upon exiting lab	
bromide (I)	Causes seri irritat	ious eye ion	2 x 10 = 20		
	May cause re irritat	spiratory ion	2 x 5 = 10	Weigh under snorkel	
	Causes skin irritation		1 x 5 = 5	Use PPE; discard contaminated gloves immediately; wash hand upon exiting lab	
Weigh out PS-PPh <sub>2</sub> (s)	Harmful if swallowed, in contact with skin, or if		2 x 5 = 10	Weigh under snorkel: use PPE	
	Causes serious eye irritation		1 x 10 = <b>10</b>	discard contaminated gloves immediately; wash hands upor	
	May cause respiratory irritation		1 x 5 = 5	exiting lab	
Weigh out cesium	Causes seri dama	ious eye ge	1 x 10 = <b>10</b>	Use PPE; discard contaminated	
carbonate (s)	May cause respiratory irritation		1 x 5 = 5	upon exiting lab	
	Combustib	le liquid	1 x 5 = 5	Do not handle near open flame or sources of ignition	
Weigh out benzaldehyde	Harmful if sw in contact v	allowed or vith skin	1 x 5 = 5	Use PPE; discard contaminated gloves immediately; wash hand	
U	Causes skin	irritation	1 x 5 = 5	upon exiting lab	
	Toxic to aquatic life			Do not empty into drains	
Clamp vial in ball mill and Caught in ball mill			2 x 5 = 10	Use care when opening and closing the ball mill	
Hazards Checklist [Note: 1 Descriptions in APPENDI	This section can [ D.]	n be modifi	ed, as needed. See Table	P-1: Common Hazards and	
Can someone be exposed to a	hemicals? Yes	If so, what Ingestion	is the nature of the chemi and inhalation hazards; e	cal hazard? ye and skin irritation	
Can someone slin trin or fal	Can someo	ne injure someone else? Y	ns		

### <u>Identify hazards</u> → <u>Analyze risks</u> → Select controls



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Source: http://www.cdc.gov/niosh/topics/hierarchy

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# **ELIMINATION AND SUBSTITUTION**

The San Destin Declaration: 9 Principles of Green Engineering\*

- Engineer processes and products holistically, use systems analysis, and integrate environmental impact assessment tools.
- Conserve and improve natural ecosystems while protecting human health and well-being.
- 3. Use life-cycle thinking in all engineering activities.
- 4. Ensure that all material and energy inputs and outputs are as inherently safe and benign as possible.
- 5. Minimize depletion of natural resources.
- 6. Strive to prevent waste.
- Develop and apply engineering solutions, while being cognizant of local geography, aspirations, and cultures.
- Create engineering solutions beyond current or dominant technologies; improve, innovate, and invent (technologies) to achieve sustainability.
- 9. Actively engage communities and stakeholders in development of engineering solutions

\*Abraham, M.; Nguyen, N. "Green engineering: Defining principles" – Results from the Sandestin conference. *Environmental Progress* 2004, 22, 233-236.DOI: 10.1002/ep.670220410



Meeting was supported by EPA, NSF, DOE (Los Alamos National Lab), and the ACS GCI.

"How can we tell if what we're doing is actually greener?"

**Green Chemistry Metrics** 



### How interested are you in a Green Chemistry metrics tool that incorporated job hazard assessment considerations?

- Very interested
- Somewhat Interested
- Neither interested or disinterested
- Somewhat disinterested
- Very disinterested

# WASTE MINIMIZATION





Leahy, Kendra; Mack, Anthony; Mack, James. "An EcoScale Comparison of Mechanochemistry and Solution Based Reactions." Green Technologies for the Environment. Obare et. al. ACS Symposium Series; American Chemical Society: Washington, DC, 2014. 129-137. Print.

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### **MEASURING WASTE MINIMIZATION - THE ECOSCALE**

Parameter	Penalty points		
	(100 0( + 10/0	5. Temperature/time	
I. field	(100 – %yield)/2	Room temperature, < 1 h	0
2. Price of reaction components		Room temperature, < 24 h	1
(to obtain 10 mmol of end product)		Heating, < 1 h	2
Inexpensive (< \$10)	0	Heating. >   h	3
Expensive (> \$10 and < \$50)	3	Cooling to 0°C	4
Very expensive (> \$50)	5	Cooling $\leq 0^{\circ}$ C	5
3. Safety <sup>a</sup>		6 Workup and purification	5
N (dangerous for environment)	5	Nene	0
T (toxic)	5		0
F (highly flammable)	5	Cooling to room temperature	0
E (explosive)	10	Adding solvent	0
F+ (extremely flammable)	10	Simple filtration	0
T+ (extremely toxic)	10	Removal of solvent with $bp < 150^{\circ}C$	0
4 Technical setup	10	Crystallization and filtration	1
Common setup	0	Removal of solvent with bp > 150°C	2
Instruments for controlled addition of		Solid phase extraction	2
chemicals	1	Distillation	3
Linear ventional activation technique	2	Sublimation	3
Disconventional activation technique	2	Liquid-liquid extraction <sup>e</sup>	3
Pressure equipment, > 1 atm <sup>4</sup>	3	Classical chromatography	10
Any additional special glassware	I .	017	
(Inert) gas atmosphere	I		
Glove box	3		

Van Aken, Koen; Strekowski, Lucjan; Patiny, Luc. "EcoScale, a semi-quantitative tool to select an organic preparation based on economical and ecological parameters." Ballstein J. of Org. Chem. 2006, 3. Leahy, Kendra; Mack, Anthony; Mack, James. "An EcoScale Comparison of Mechanochemistry and Solution Based Reactions." Green

Technologies for the Environment. Obare et. al. ACS Symposium Series; American Chemical Society: Washington, DC, 2014. 129-137. Print.

### **MEASURING WASTE MINIMIZATION - THE ECOSCALE**

Parameter I. Yield 2. Price of reaction components (to obtain 10 mmol of end product)		rer Penalty points (100 - %yield)/2 of reaction components ain 10 mmol of end product)		5. Temperature/time Room temperature, < 1 h Room temperature, < 24 h Heating < 1 h		
Inexpensive	(< \$10)	0		LI.		
Expensive ( Very exper 3. Safetya		So	olution		Mechano	chemistry
N (dangerc T (toxic)	Total Penalty Points		65			23
F (highly fla E (explosiv	EcoScale rating	100-65	35		100-23	77
F+ (extrem T+ (extren	Overall Assessment		Inadeq	uate		Excellent
<ul> <li>Technical sc.</li> <li>Common set Instruments chemicals<sup>b</sup></li> <li>Unconventio Pressure equ Any addition</li> </ul>	-r tup for controlled addition of anal activation technique <sup>c</sup> aipment, > 1 atm <sup>4</sup> al special glassware	0   2 3 		Rem Solic Dist Subl Liqu Clas	oval of solvent w I phase extractior illation imation id-liquid extractio sical chromatogra	ith bp > 150°C n on <sup>e</sup> ophy
(Inert) gas at Glove box	mosphere	 3				

Van Aken, Koen; Strekowski, Lucjan; Patiny, Luc. "EcoScale, a semi-quantitative tool to select an organic preparation based on economical and ecological parameters." *Bollstein 1. of Org. Chem.* 2006, 3. Leahy, Kendra; Mack, Anthony; Mack, James. "An EcoScale Comparison of Mechanochemistry and Solution Based Reactions." *Green* 

Leahy, Kendra; Mack, Anthony; Mack, James. "An EcoScale Comparison of Mechanochemistry and Solution Based Reactions." Green Technologies for the Environment. Obare et. al. ACS Symposium Series; American Chemical Society: Washington, DC, 2014. 129-137. Print.

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# **SUMMARY**

- Risk = hazard x exposure
- Determine scope (use SDS!)
- Assemble your team
- Conduct a hazard assessment
  - Assigning risk ratings
  - Job hazard analysis
- Select controls
- Green engineering principles
- Green chemistry metric: EcoScale





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# **ACKNOWLEDGMENTS**

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- Prof. Neil Ayres

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- Marta Gmurczyk
- Mary Kirchhoff

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#### Undergraduates:

Preston Carr Kingsley Benson





- Rashad Pace
- Nina Trankina









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# **KEY CHEMICAL SAFETY REFERENCES**

Audience	Technical Resources	Cultural Resources
High school and undergraduate teaching labs	<u>NFPA 45 requirements for</u> <u>instructional and educational</u> <u>labs</u> , 2015	<u>Guidelines for Chemical Lab</u> <u>Safety in Secondary Schools</u> , ACS 2016
Mentored research labs (REU, CURE, similar programs)	Safety in Academic Chemistry Laboratories, 8th edition ACS 2017	<u>Creating Safety Cultures in</u> <u>Academic Institutions</u> ACS, 2013
Supervised research (graduate school)	<u>Guidelines for Chemical Lab</u> <u>Safety in Secondary Schools</u> , ACS 2016	<u>A Guide to Implementing a</u> <u>Safety Culture in our</u> <u>Universities</u> APLU, 2016
Research leadership	Prudent Practices in the Laboratory National Academies Press 2011 Hazard Assessment in Research Laboratories ACS, 2016	Safe Science National Academies Press, 2014 Safety Guidelines for the Chemistry Professional ACS DCHAS / CCS, 2017

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# **KEY GREEN CHEMISTRY REFERENCES**

Audience	Technical Resources
	EcoScale green chemistry metric
Laboratory Researchers	ACS Green Chemistry Institute
	<u>"An EcoScale Comparison of</u> <u>Mechanochemistry and Solution Based</u> <u>Reactions,"</u> 2014



This ACS Webinar is co-produced by the ACS Division of Chemical Health and Safety and the ACS Green Chemistry Institute

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http://bit.ly/GreenNano





#### **Experts**



James Hutchison University of Oregon



Howard University

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Joe Fortunak

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#### Full Day: How to be a More Effection

Hygiene Officer Reactive Chemical Management for Laboratories & Pilot Plants Laboratory Safety – Bevond The Day: ACE Resources to Teach Lab Safety mg for secondary school audiences, on for undergraduates) bib Extraction Workshop (morning) bib Sahavies Morector

(morning the inconsist to Teach Lab Ba alternoon for undergraduates) Cannabis Analysis Workshop (morning Cannabis Analysis Workshop (afternoon

The division is dedicated to supporting the efforts of chemical manufacturers, industrial and academic researchers, and science teachers at all levels to work for a safe and healthful work environment. Through our technical symposia, the Division's Journal, the *Journal of Chemical Health and Safety*, our **workshops** and our **DCHAS-L listserv**, we provide a forum for scholarly health and safety research, advice and counsel from an experienced group, and support for health and safety efforts in industry and academia.

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#### Thursday, May 18, 2017

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**Creating a 21st Century Chemical Research Laboratory:** Hazard Assessments and Fundamentals



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This ACS Webinar is co-produced by the ACS Division of Chemical Health and Safety and the ACS Green Chemistry Institute

# THE TAKE HOME MESSAGE

Job Hazard Analyses and Green Chemistry metrics support each other and make for better and safer science. This is because they are both based on clear, careful descriptions of the chemical processes being conducted.





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"Darren offered a refreshing perspective on how to act as a scientist. It was a nice reminder to find positives in a negative situation. I also liked how Darren challenged the audience to be open to art (and other fields), and not to be a closedoff scientist."



**Kevin Kempton Research Associate** Innophos, Inc., ACS member for 3 years strong!

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Thursday, May 18, 2017



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