聲明

Green Laboratory Practices
綠色化學與化學安全

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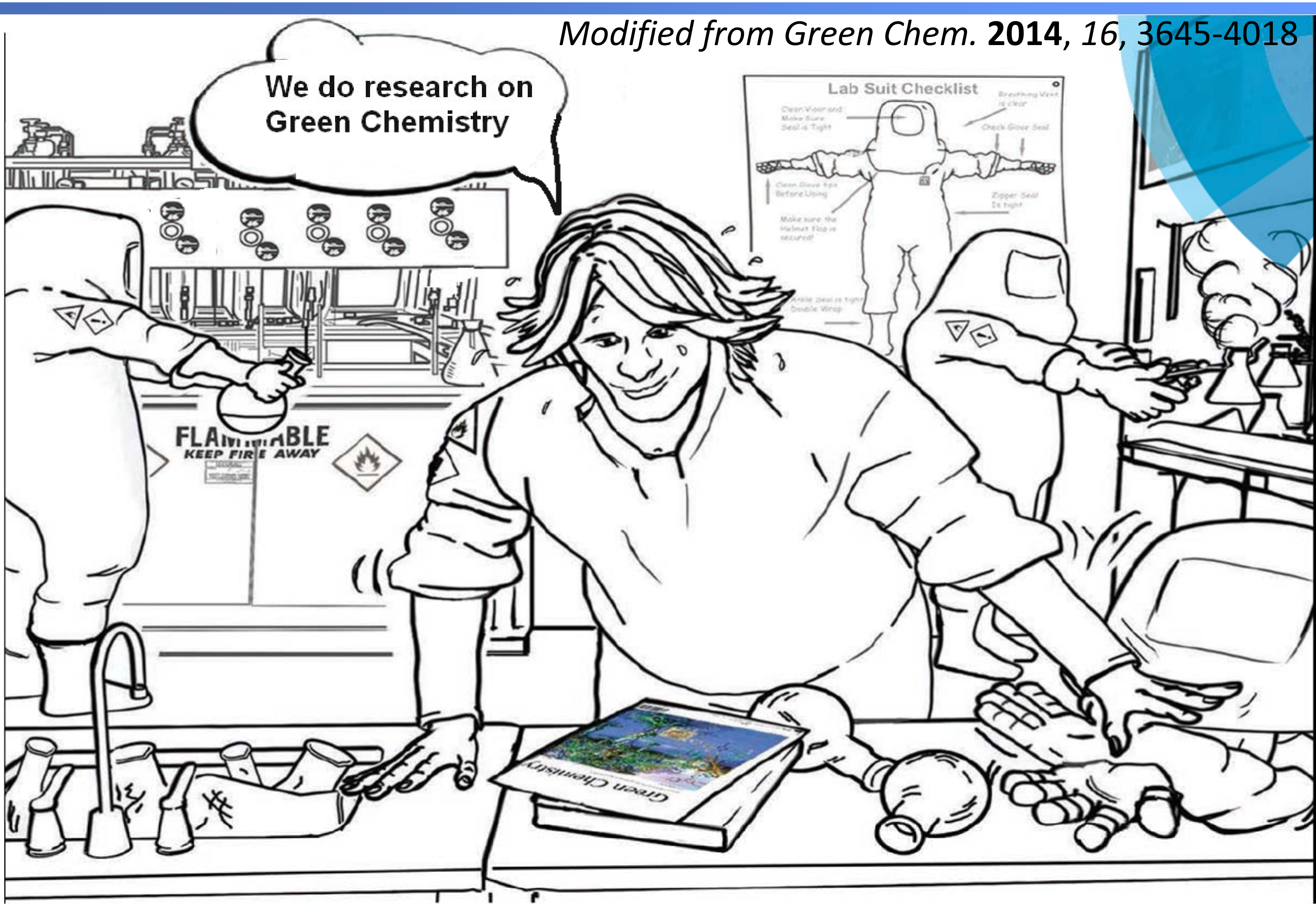
綠色化學講習會

中國化學會 2014年會

Is your lab Green?

Modified from Green Chem. **2014**, *16*, 3645-4018



Outlines of this presentation

- Safe and risk
- Create safety culture
- Severity and probability
- Human reliability, common causes and special causes for lab accidents
- The concepts of preventive and protective actions
- Understanding chemical safety levels
- Hazards in chemical research
- References


Safe and risk

12 principles of Green Chemistry

Safety is an important concept in our “Green World”

Green Chemistry

Prevention of waste generation

Atom Economy

Less Hazardous Chemical Syntheses

Designing Safer Chemicals

Safer Solvents and Auxiliaries

Design for Energy Efficiency

Use of Renewable Feedstocks

Reduce Derivatives

Catalysis

Design for Degradation

Real-time analysis for Pollution Prevention

Inherently Safer Chemistry for Accident Prevention

Dilemma

What is green, sustainable, and Safe?

- No clear cut definition, standard, or criteria for green or sustainable
- Sounds positive to environmental and/or societal
- Who has the authority to define “green”?

How about “Safe”?

Reduce risk = Safe ?

Good or Bad

Making fire: > 10,000 years ago (Before new Stone Age)

Fire can generate "Heat" and "Light"

Good

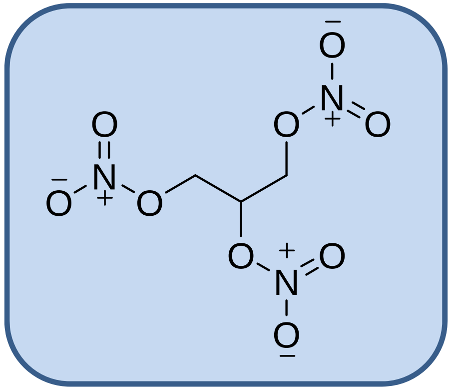
Campfire: Your favorite
Because it is under control

Bad

Forrest fire: Your nightmare
Because it is out of control

Good or Bad

Nitroglycerin
Ascanio Sobrero in 1847
Alfred Nobel since 1858.



Bad: Instability
Five serious explosion during 1864-1866, killing Nobel's young brother Emil Oskar Nobel and others

Good: After desensitization, one can make dynamites or plastic explosives, which are benefit for construction industries
Examples
(a)by mixing nitroglycerin with inert absorbents particularly *"kieselguhr,"* or diatomaceous earth.
(b)by mixing nitroglycerin with guncotton and petroleum jelly.

An explosion in an inorganic lab

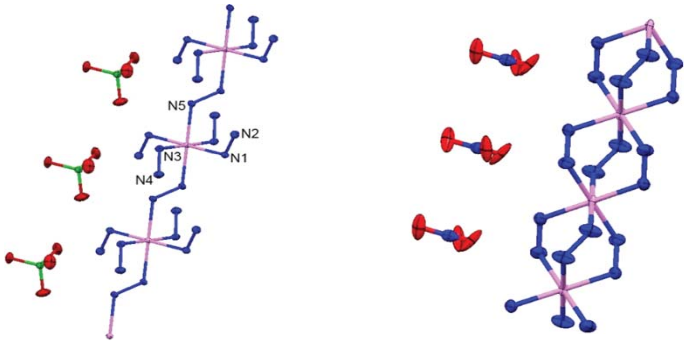
Scaling up the process

January 2010 Texas Tech Laboratory Accident

Preston Brown, a senior graduate student and another year-one student synthesized a derivative of nickel hydrazine perchlorate (NHP)

- Had no formal training with the material/hazards
- No personal protection equipment (no shield, on bench top, not even safety glasses)
- Exceeded the 100 mg limit and scaled up to 10 g.
- They believed that keeping NHP wet with a solvent (hexane) would prevent it from exploding.
- When 5 g of NHP was pressed and grinded by the pestle, it detonated.
- His left hand severely injured by the force of the explosion, causing the loss of three fingers, perforation of his eye, and cuts and burns to other parts of his body.

They had near-misses experience before.



$Ni(N_2H_4)_5(ClO_4)_2$ $Ni(N_2H_4)_3(NO_3)_2$

RSC : Ionic polymers open door to greener, safer explosives. (JACS 2012, 1422-1425.)

Another Scenario

On June 17, 2014 an explosion in a chemistry lab at the University of Minnesota injured graduate student Walter Partlo. He was making trimethylsilyl azide, starting with 200 g of sodium azide. The incident originated in lack of hazard awareness

Tolman, Sitek, and other investigators have not been able to definitively identify what went wrong with the reaction, Tolman says. One explanation is that the explosion was from hydrazoic acid, which could have formed from wet PEG providing water to react with sodium azide, or the PEG itself reacting with sodium azide. Another explanation is that the sodium azide overheated.
More important than the reaction, Tolman emphasizes, is the deeper root cause of the incident: insufficient recognition of the reaction's hazards. Warnings included with literature protocols were "pretty lame"…. He has set a limit of 5 g. …

http://cenblog.org/the-safety-zone/2014/07/more-details-on-the-university-of-minnesota-explosion-and-response/

Short summary

Principle 12: Inherently Safer Chemistry for Accident Prevention – Choose substances and the form of a substance used in a chemical process to minimize the potential for chemical accidents, including releases, explosions, and fires.

However, in facts, a chemical laboratory working on "Green Chemistry" may not green or safe. The safety issue depends on many other factors..., like driving a car on highway.

whether we understand risks and hazards, and knowing the way of controlling the risk and hazards

Our Destiny depends on whether we can have the dino chained

http://www.zazzle.com/to_the_pub_dinosaur_t_shirt-235476849649830389

Hi! Dino.　Wait here. I'm going to the Pub.


Safety Culture

Accidents or Disasters

Accidents or Disasters? Dependent on our attitude.

Creating Safety Cultures in Academic Institutions

Committee on Chemical Safety

http://www.acs.org/content/acs/en/about/governance/committees/chemicalsafety.html

Understanding probable factors behind accidents

The Weaknesses on Human Reliability

Common-Causes for accidents

Special-Causes for accidents

Factors affecting the quality of safety management

Emergency Preparedness

Budgetary control

Damage control capability

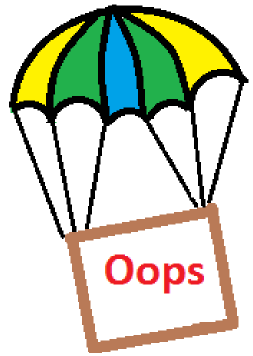
Maintenance

Creating Safety Cultures in Academic Institutions

What is the essence of “Green”?

- Life is recycled each year to keep the world stainable -

How could you keep old planes fly?
Why do be need a parasuit?



Why do we need safety motor helmet? Why do we put on sit-belt?
Why do we have our car maintenance regularly?
Just because we believe that we need them.

 Artwork from http://shirt.woot.com/blog/post/four-seasons-in-one-day

Elements of Strong Safety Cultures – a positive attitude

Leadership and management. —safety must be clearly defined from the highest levels of the administration, down to individual faculty and staff (students).

Teaching laboratory and chemical safety— emphasizes teaching "critical thinking" skills in laboratory and chemical safety should be taught.

Strong safety attitudes, awareness, and ethics—Long-term efforts through continuous emphasis on safety. Teaching (and learning) safety is an ethical responsibility. The Safety Ethic reflects the proper attitude of valuing safety.

Learning from laboratory incidents — Study, report and investigate incidents.

Establishing collaborative relationships — Trust between faculty members; administrative staff; students; postdoctoral scholars; and Environmental, Health, and Safety staff—as well as public emergency responders.

Promoting and communicating safety —Demonstrating safety practices through personal example and recognizing positive safety behaviors are important ways to promote safety.

Strong safety programs require funding— All strong safety programs require investment of substantial effort with adequate and continuous funding by institutional administrations. Identifying responsibilities for safety is a critical step in determining budgets.

Dr. Robert H. Hill, Jr., *is the Chair of the ACS Joint Board/Council Committee on Chemical Safety.*

http://www.acs.org/content/acs/en/education/students/graduate/creating-safety-cultures-in-academic-institutions.html

Facing the reality of all near-misses cases

Job 1. Don't ignore any near-misses

Near-misses, or near-hit means luckily nothing happened – this time, but it was an incident.

It is valuable experience for prevention of accidents.

Warning: They are lagging indicators of safety

Just paying lip-service to the concept of safety rather than actually backing it up in practice

2012 survey of safety in US academic laboratories (about 2400 researchers)

86%	They believed their laboratories were safe places to work.
94%	Senior researchers felt that appropriate safety
80%	Working in their laboratory alone at least once a week !!!!
54%	Sometimes didn't wear a lab coat.
40%	Not to have received safety training on specific agents or hazards.
60%	Thought that safety in their chemical laboratories could be improved.
30%	Aware of at least one 'major' injury occurring in their laboratory.

Safety first? 29 May 2014, by Jon Evans
http://www.rsc.org/chemistryworld/2014/05/safety-first

Why safety being overlooked?

Accident Pyramid Diagram by the US safety researcher, Frank Bird, 2013-MSHA

Sometimes only when several mistakes happen coincidentally would lead to a disaster. Since the probability is low, many PIs and researchers simply ignore the risk.

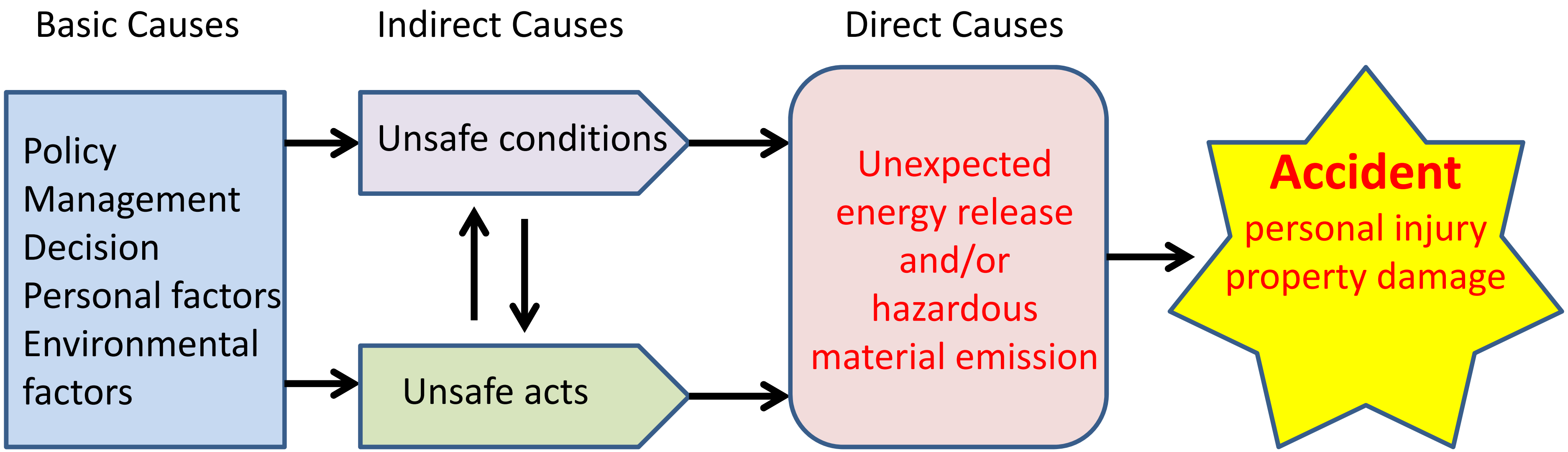
Example

Factors that lead to gas explosion, which caused serious damage and kills

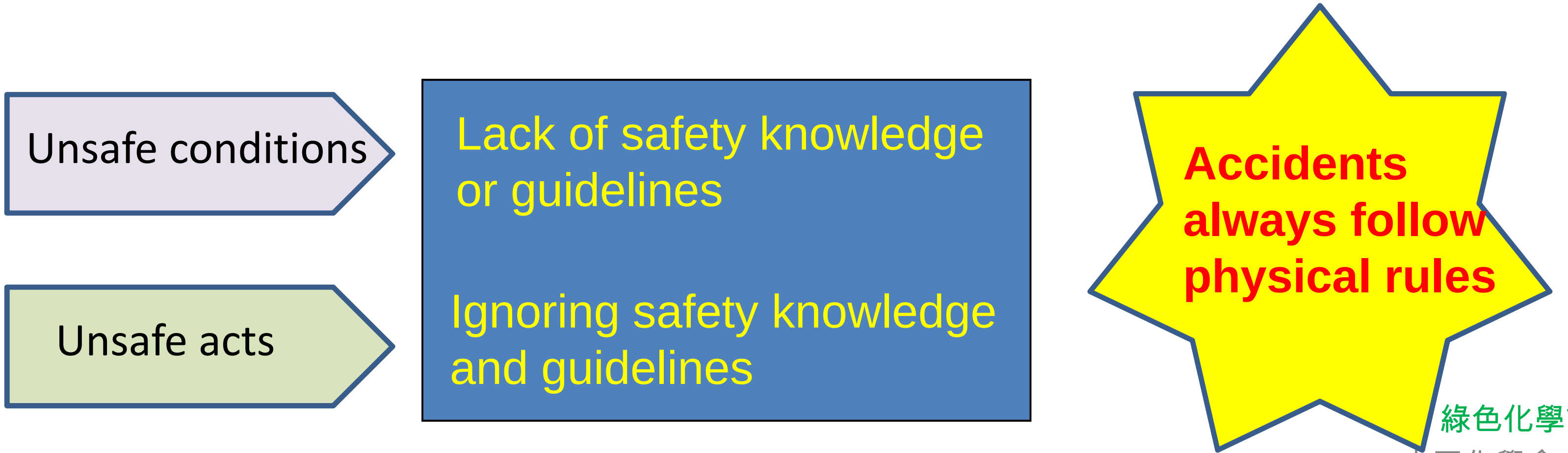
(1) Inappropriate location of pipeline
(2) Lacks of pipeline information
(3) Violate the construction guidelines
(4) Lacks of damage control information
(5) Lacks of maintenance
(6) Ineffective evacuation operation etc.

However, when all check points go wrong coincidentally, disaster becomes inevitable . If any one of these can be eliminated, the tragedy could be avoided.

Accident Analysis - Improvements through tragedy



U.S. Department of Labor, Mine Safety and Health Administration Safety Manual No. 10 Accident Investigation, 1990



Difficult to change principal investigators' attitudes

UCLA

Died of burns

Yale

Died of suffocation

Sheharbano Sangji (2008/12/29) Michele Dufault (2011/4/14)

Yet …have not seen a significant shift in the behaviour of bench scientists or the attitudes of lab heads …to improve safety culture. ….All too often, researchers in laboratories around the country still work alone, and without proper supervision or protection.

Fatality adds further momentum to calls for a shake-up in academic safety culture.
Richard Van Noorden

It's very difficult to change principal investigators' attitudes

James Gibson, UCLA's director of environmental health and safety.

In many cases, academic freedom is more important than safety

Jim Kaufman, president of the Laboratory Safety Institute in Natick, Massachusetts.

Discussion about Sheharbano Sangji's death

Brenna Arlyce Brown, who received her PhD in chemistry in 2013 and is currently working in business development for a research funding organization. She is working on setting up a safety consulting business

… My old PhD boss was sure this can't happen in our lab-then he found out that I used *t*BuLi-things soon changed ." This of course sparked questions: "What changed?" "Why didn't he know that you were using the chemical?" Twitter's 140 characters were just not enough to answer fully. …

… Following the incident at UCLA, it became apparent that they are necessary and that, yes, they are the principal investigator's (PI's) responsibility—the PI is the manager. …

Academic lab safety: One chemist's observations
http://cenblog.org/the-safety-zone/2014/08/academic-lab-safety-one-chemists-observations/

Endless Accidents in Laboratory

Laboratories are potentially dangerous work environments for exploring unknowns.

....Since 2001, **more than 120 university lab accidents have caused injuries**, millions of dollars in damages, and **one death**, according to the federal **Chemical Safety & Hazard Investigation Board** (CSB)… (2011)

….There were nearly **10,000 accidents in research laboratories in 2005** injuring nearly 2 out of every 100 researchers, (i.e. injuring 2% of researchers) according to **government statistics**. ….

- Explosion in a chemistry lab at the University of Minnesota (6/2014)
- University of Texas Gas Explosion/Projectile (6/2012)
- Princeton Solvent Explosion (5/2012)
- VA Medical Center San Francisco Neisseria meningitidis Infection (4/2012)
- University of Florida Sodium Azide Explosion (1/2012)
- University of Chicago Bacillus cereus Infection (8/2011)
- Yale Lathe Accident (4/2011)
- University of Missouri Hydrogen Explosion (6/2010)
- Texas Tech Nickel Hydrazine Perchlorate Explosion (1/2010)
- University of Chicago Yersina pestis Infection (9/2009)
- UCLA tert-Butyllithium Fire (12/2008)
- Ohio State Hexane Lab Fire (4/2005)
- Dartmouth Dimethylmercury Exposure (8/1996)

Summarized by OSEH, Univ. of Michigan (http://www.oseh.umich.edu/research/lab-accidents.shtml)

Total risk, a function of Severity and Probabilistic risk

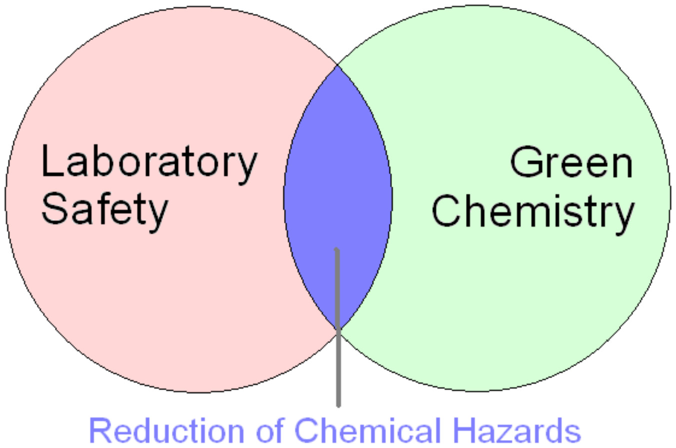
Risk in a feasible detrimental outcome of an activity or action is determined by

Total risk (expected loss) = Σ f(Severity; Probability)

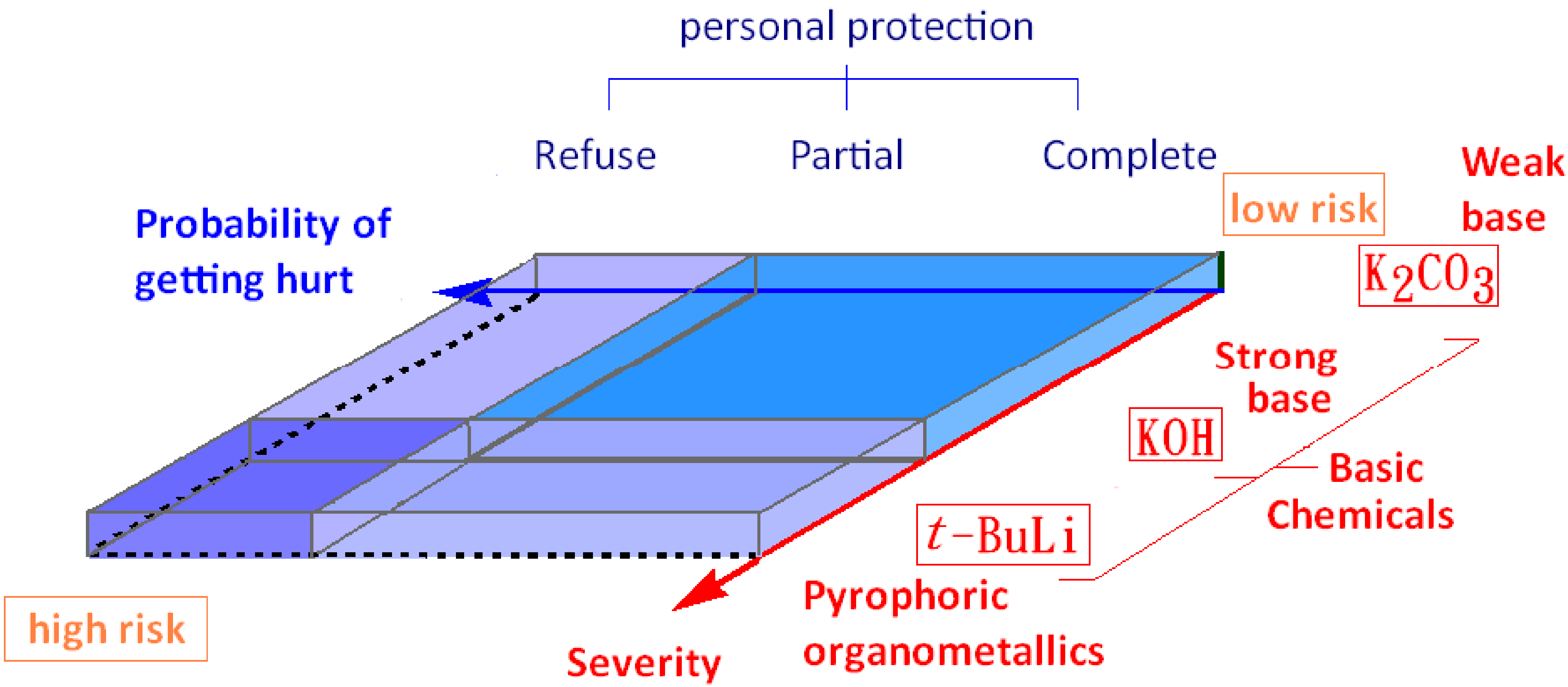
e.g.
Estimated total damage each year = the number of people potentially hurt or killed in each accident x occurrence frequencies

Reduce reaction scale → Reduce severity in each accident

Follow SOP or guidelines → Reduce the probability of human errors



Severity and Probabilistic risk



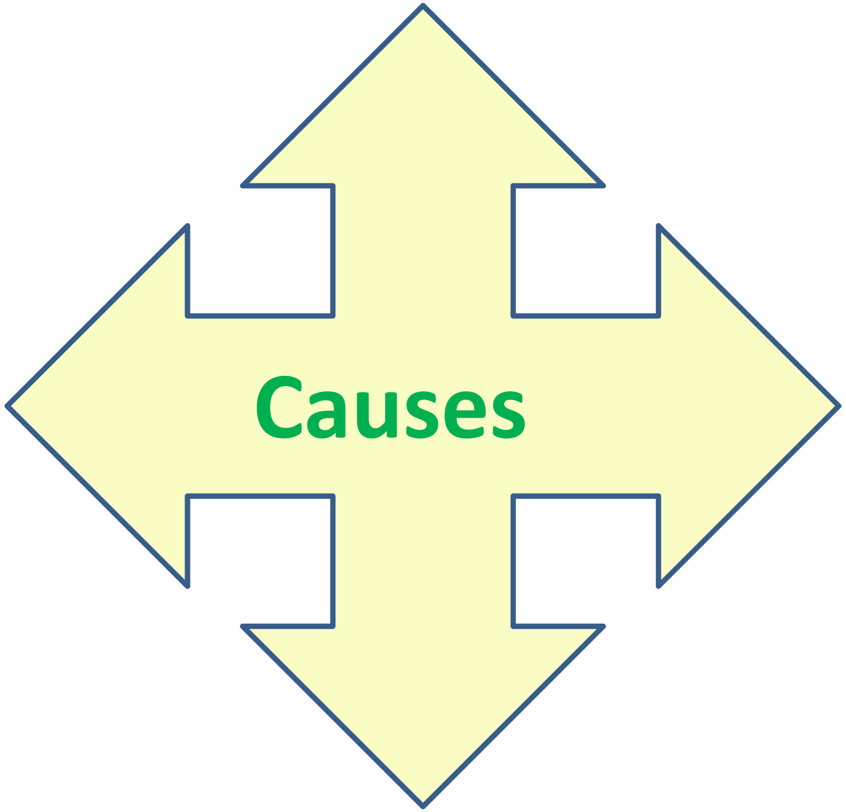
The reaction scale is a matter of severity

Walter Partlo in Minnesota was making trimethylsilyl azide, starting with 200 g of sodium azide. The incident originated in lack of hazard awareness, but Tolman has set a limit of 5 g. (One possible reason is the PEG used was wet, generatingHN_3)

Preston Brown scaled up to 10 g in the synthesis NHP derivatives, and exceeded the 100 mg limit.

The American Chemical Society (ACS) originally published *Less Is Better* in 1985. Buy less-Store less-Use less, reducing the scale of laboratory processes reduce the severity in an accident.

Applying Green Chemistry Principles to Laboratory Operations Peter A. Reinhardt, Yale University


Causes

How to prevent accidents or disasters -reducing probabilistic risks

Accidents or Disasters? Dependent on our attitude.

- Creating Safety Cultures in Academic Institutions
- *Committee on Chemical Safety*
- *http://www.acs.org/content/acs/en/about/governance/committees/chemicalsafety.html*

Understanding probable factors behind accidents

- The Weaknesses on Human Reliability
- Common-Causes for accidents
- Special-Causes for accidents

Factors affecting the quality of safety management

- Emergency Preparedness
- Budgetary control
- Damage control capability
- Maintenance

Four steps of learning for frontline laboratory researchers

Frontline laboratory workers should remember the four steps of learning:

- Unconscious incompetence: You don’t know what you don’t know.
- Conscious incompetence: You realize you don’t have adequate knowledge.
- Conscious competence: You are able to function safely and effectively.
- Unconscious competence: You are very knowledgeable and experienced regarding the subject at hand.

If a person does not understand the hazard or why a control was put into place, they are not likely to recognize how a change to the hazard or control could be significant. Also, while risk is measurable, it is also subject to personal interpretation. Everyone has a different risk perception.

Identifying and Evaluating Hazards in Research Laboratories, ACS, 2013

Understanding and evaluating the safety

- Establish **thresholds** (and authority to authorize tasks that exceed a threshold)
  X-ray generating device, biological work, controlled substances; scale-up of energetic materials, laser alignment, and use of engineered nanomaterials….
  Ensure the thresholds are understood ……
- Use **peer reviews** (To observe and ask questions)
- Routinely conduct reviews of laboratory activities.
- Look for changing work conditions and ask questions about processes.
- Report and **discuss incidents, near misses and close calls**.
- Include information on hazards in notebooks, papers, and presentations, so the new knowledge is **disseminated to a wider audience**.

Human Reliability and Lab Safety

Human Reliability can be affected by many factors including:
age
state of mind
physical health
attitude
emotions
propensity for certain common mistakes errors and cognitive biases,

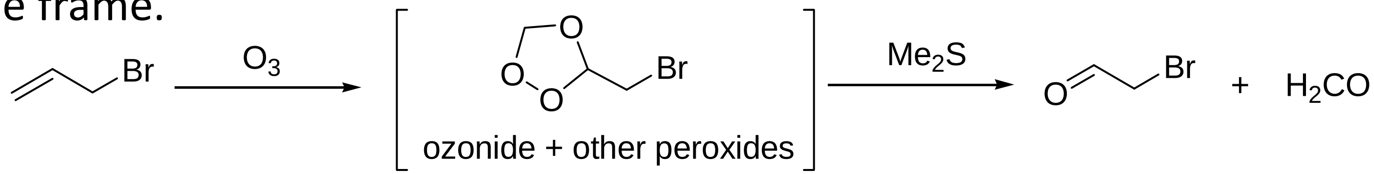
Examples of human reliability cause

- Get tied
- Get sick
- Bad temper after quarrel
- Absent mindedness
- Ignorance about safety regulations and guidelines
- Eat or play in research area
- Misunderstanding the operation procedure
- Inappropriate operation of experimental setups or tools

Inexperience students keep enrolling; Senior students keep leaving
We need to have continuous safety education to maintain the "dynamic equilibrium"

An explosion in a synthetic organic lab
misunderstanding the operation procedure

Scenerio: An OSU grad. student was distilling a mixture of CH_2Cl_2 and crude material from an ozonolysis of allyl bromide, which he mistakenly thought was bromoacetaldehyde. Unknown to the student, he was trying to distill a mixture of peroxides (that resulted from the ozonolysis). An explosion occurred when the temperature reached 50 ^oC. The explosion destroyed the heating mantle and the ceramic top of the stirrer/hot-plate. The ceramic top fragmented and sent chards into the face, chest, shoulders, and hands of the student. One chard hit the left lens of his safety glasses with such force that it shattered but remained within the frame.



John Herrington
Health and Safety Officer , College of Math and Physical Sciences, Ohio State University
http://www.chemistry.ohio-state.edu/ehs

× Wrong handling (Perhaps misunderstanding the operation procedure. Reduction of the peroxides with Me_2S is necessary according to the published procedure (*Organic Preparations and Procedures International: The New Journal for Organic Synthesis Volume 25, Issue 4, 1993)*

- × Fumehood Sash open (violate safety guidelines)
- √ Safety glasses (save his eye)

Simple things can cause great harm

Over 40 % of fire accidents caused by electrical incidents (Taiwan statistics)

Simple chemicals lead to serious damage

- $NaOH/H_2SO_4/HNO_3$ (Corrosive)
- $H_2O_2/H_2SO_4/NaOH/$ catalysis (explosion)
- $KMnO_4/H_2SO_4/$Organic compounds (fire)
- Mixing organic waste with waste acids (explosion)
- Overheated organic solvents (explosion)

Mixing $KMnO_4/H_2SO_4/$toluene causes fire

Extensively use corrosive acids causing electrical short circuit and fire accidents

Mixing organic waste with waste acids causes explosion

Examples of Human Reliability Problems

Ignoring safety regulations

Inappropriate electrical setups

Drinks in research area

Poor Lab management

Common-cause for Lab Accidents

Examples of Common causes (poor maintenance and management)

- Lack of clearly defined standard operating procedures
- Inappropriate procedures
- Poor lab and experimental area design
- Normal wear and tear, and poor maintenance of machines
- Poor working conditions, e.g. lighting, noise, dirt, temperature, ventilation, ambient temperature, and humidity
- Substandard raw materials
- Measurement error
- Quality control error etc.

Wearing of the drying oven

Special-cause variation for Lab Accidents

Special-cause always arrives as a surprise

Special causes

- Faulty Instrument or machine malfunction
- Fall of cabinet in a laboratory
- Power surges
- Earthquake
- Fire accident
- Unexpected water leak or water shut off
- Unexpected outcome from chemical research

EHS, NTU

Tohoku University after earthquake
http://cenblog.org/the-safety-zone/2011/03/laboratory-damage-from-japan-earthquake/
http://msysb.material.tohoku.ac.jp/english/earthquake_e.htm

How to prevent accidents or disasters -reducing probabilistic risks

Accidents or Disasters? Dependent on our attitude.

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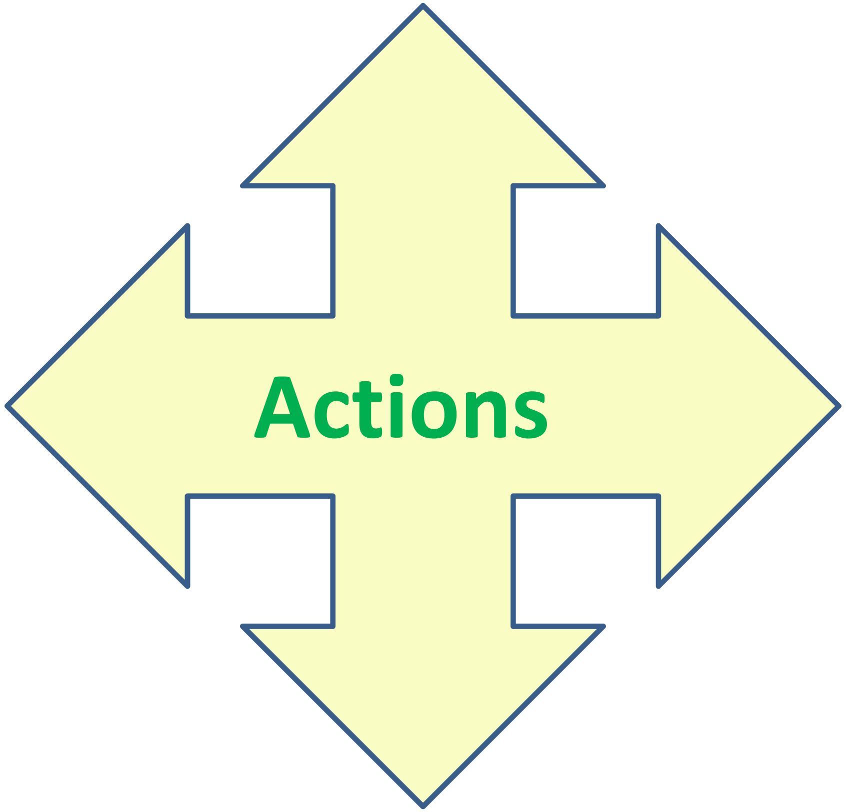
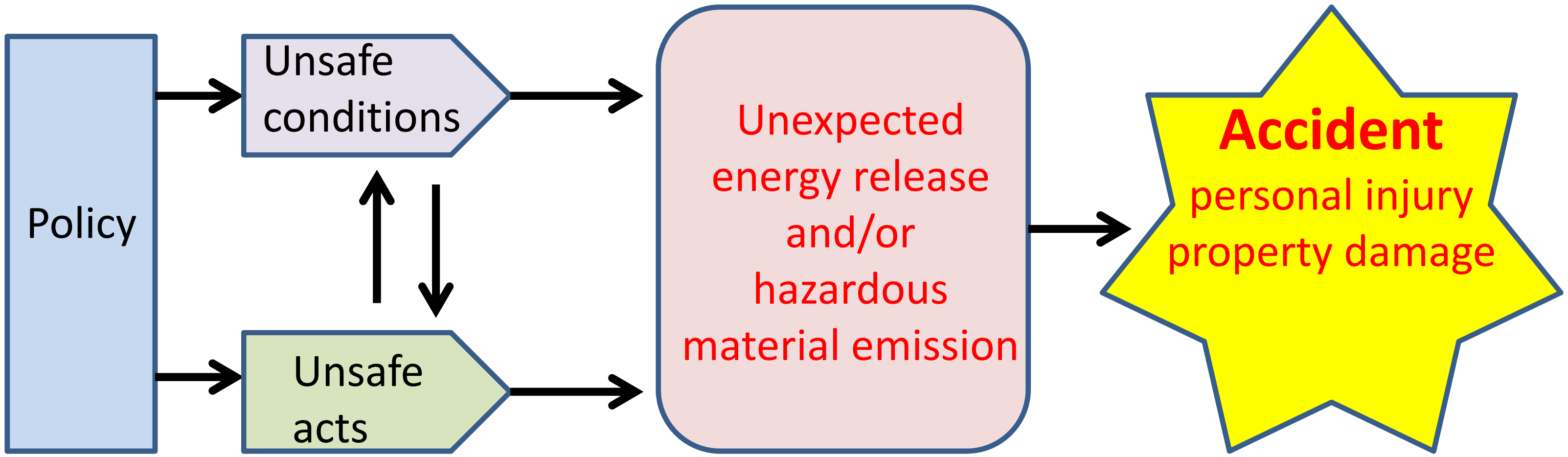

Actions

The quality of safety management



Preventive and corrective actions to reduce unsafe conditions or acts

Personal protection and damage control reduce injury and property damage

The quality of safety management

Laboratory accident prevention and Emergency Preparedness

Foundation of this working knowledge

- Hazard recognition and evaluation
- Risk evaluation
- Elimination / minimization of identified risks
- Attention to tasks being performed.

Reference: How Can I Prevent Laboratory Accidents? Kathryn G. Benedict, MS CSP, Pfizer Global Research and Development, Ann Arbor, Michigan 48105

Good planning, training, and emergency preparedness

When chemical accidents cause harmful, or even catastrophic results, such as toxic fumes, fires, and explosions.

Enough preparedness enable:

- fast response to a crisis
- appropriate reaction to a wide spectrum of emergencies
- damage control
- laboratory rescue

Preventive and corrective actions

When accident happens, there might be no time to think before making a decision.

- Preparation-planning for emergency drills and practices
- Lab inspection
- Risk assessment

Lab inspection	Risk assessment
• Tidiness • Conditions and maintenance of facilities • Training and Education • Laboratory ventilation (smell) • Safety equipments and tools • Chemical substances and waste storage (chemical inventory and management) • Biological safety • Radiation safety	• The scope of the project or experiment. • Substances, processes/techniques and disposal of waste. • Determine the potential hazards involved: • Evaluate the level of risk: • Determine the actions and controls to be taken • Continuous monitor and review

This give a chance to reset the lab conditions regularly

Do forget to allocate budget for maintenance and replacement

Protective actions in Chemical Laboratory

https://osha.europa.eu/en/publications/e-facts/efact20

We may not be able to stop the accident for sure, we have to, at least, reduce the damage

Laboratory safety policy

- Mandatory use of **personal protective equipment (PPE)**
- Mandatory **buddy system**
- MSDS
- Separate storage of incompatible chemicals and waste
- Appropriate dress guidelines
- Guidelines for poison chemical safety and emergency treatment
- Emergency personal **contact information**

Chemical safety equipment and tools

- Safety goggles
- Lab coats
- Shoes
- Gloves
- Masks
- Shields
- Fumehoods and Ventilation
- Emergency showers and eyewashers
- Fire extinguisher, sand, and blanket
- First-Aid kit

The most basic investment

Personal protective equipment

Safety goggles, dress and shoes

Personal protective equipment

Masks and gloves

Masks






Chemical resistant gloves


Nitrile


nitrile hybride


long


Rubber


viton


PVC

Surgical and PE gloves


Surgical Gloves

PE Gloves


PE Gloves


Duo Gloves

Cases of Insufficient protection

The incident occurred on August 14, 1996. Protective gloves in use at the time of the incident provided insufficient protection, and exposure to only a few drops of Me_2Hg absorbed through the gloves proved to be fatal after less than a year for Prof. Karen Witterhan.

Later tests showed that Me_2Hg can in fact permeate latex gloves and enter the skin within about 15 seconds.

Prof Karen Witterhan died on June 8 1997

Prof. Karen Witterhan
Dartmouth College

Elizabeth Griffin, a 22-year-old employee at a US primate research centre died of complications from the herpes B virus. Her eye was splashed with an unknown substance as she was moving a caged rhesus. This substance inflamed her eye and she died four weeks later. She was not wearing eye goggles because this should be considered a low-risk activity.

Rhesus Macaque

https://osha.europa.eu/en/publications/e-facts/efact20

Cases of Insufficient protection

In 1995, a seemingly small-scale spill of HF killed a technician in Australia. He died from multi-organ failure two weeks after the incident.

- He was alone.
- He worn only rubber gloves and sleeve protectors but nothing covering his lap
- He was working in a crowded fume hood.
- The lab had no emergency shower, nor any calcium gluconate gel antidote available.

David Bradley science journalist
http://www.sciencebase.com/science-blog/incidents-and-accidents.html

Hydrofluoric acid is a serious systemic poison. It is highly corrosive. Its severe and sometimes delayed health effects are due to deep tissue penetration by the fluoride ion. The surface area of the burn is not predictive of its effects.


Safety Levels

Chemical Safety Levels

Chemical exposure hazard:
acute (immediate) or chronic (delayed) health effects

how much
how long and how often
how and where the material gets in or on the body (inhalation, absorption, ingestion,accidental needle stick).
health effects (transient, persistent, or cumulative; local or systemic).

Identifying and Evaluating Hazards in Research Laboratories, ACS, 2013

Classification of laboratory according to Chemical Safety Levels

• **CSL Level 1:** (Common Examples: Instrumentation Labs)
Minimal chemical or physical hazard. No concentrated acids or bases, toxics, carcinogens or teratogens. Less than 4 liters of flammable liquids. No fume hood required. Typical examples include science undergraduate teaching and demonstration labs, research lab with minor chemical usage, laser labs (below Class 2B), and microscopy rooms.

• **CSL Level 2:** (Common Examples: Teaching Labs, Analytical Labs, or Bio-Labs)
Low chemical or physical hazard. Small amounts, less than 1 liter of concentrated acids or bases, possesses none or limited amounts of toxic or high hazard chemicals. Less than 40 liters of flammable liquids in use. May need a fume hood for some activities. Typical examples include: chemistry/biochemistry teaching and demonstration labs and standard biomedical research labs.

Identifying and Evaluating Hazards in Research Laboratories, ACS, 2013

Classification of laboratory according to Chemical Safety Levels

- **CSL Level 3:** (Common Examples: Chemical Research Labs)

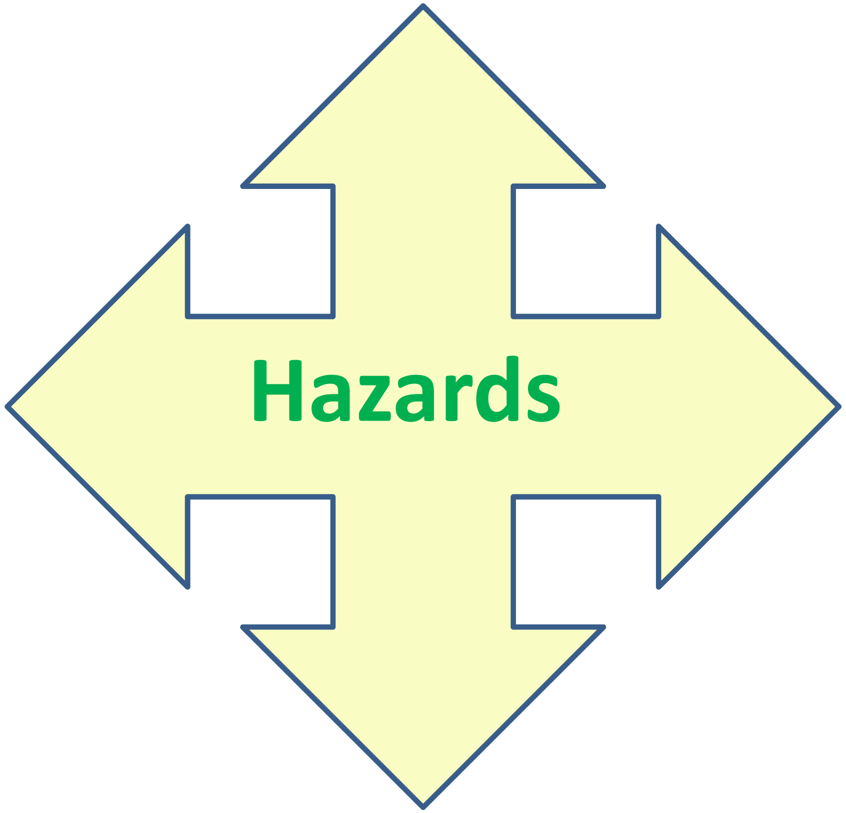
Moderate chemical or physical hazard. Lab contains concentrated acids, bases, toxic, other high hazard chemicals, or cryogenic liquids. Carcinogens or reproductive toxins are handled. Corrosive, flammable, toxic compressed gases in cabinets or fume hoods. Larger volumes of flammable liquids in the lab. Special hazards in limited quantities may be in the lab with Environmental Health and Safety (EH&S) approval (for example, hydrofluoric acid, pyrophoric chemicals, or cyanides). Labs are fume hood or local exhaust intensive. Some uses of a glove box for air reactive chemicals or quality control. Examples include chemistry research, pharmacology, chemical engineering, and pathology labs, as well as other chemical-intensive research labs.

- **CSL Level 4:** (Special Chemical Labs)

High chemical or physical hazard. Work with explosives or potentially explosive compounds, frequent use or larger quantities of pyrophoric chemicals. Use of large quantities or extremely high hazard materials with significant potential for Immediately Dangerous to Life and Health (IDLH) conditions in the event of uncontrolled release or foreseeable incident. Use of glove box for pyrophoric or air-reactive chemicals.

Identifying and Evaluating Hazards in Research Laboratories, ACS, 2013

Hazards in Research Activities



Hazards in Research Activities

Examples of Hazards Commonly Identified for Research Activities	
Hazard Type	Example
Agent	Carcinogenic, teratogenic, corrosive, pyrophoric, toxic, mutagenic, reproductive hazard, explosive, nonionizing radiation, biological hazard/pathogenic, flammable, oxidizing, self-reactive or unstable, potentially explosive, reducing, water-reactive, sensitizing, peroxideforming, catalytic, or chemical asphyxiate
Condition	High pressure, low pressure, electrical, uneven surfaces, pinch points, suspended weight, hot surfaces, extreme cold, steam, noise, clutter, magnetic fields, simple asphyxiant, oxygen-deficient spaces, ultraviolent radiation, or laser light
Activity	Creation of secondary products, lifting, chemical mixing, long-term use of dry boxes, repetitive pipetting, scale up, handling waste, transportation of hazardous materials, handling glassware and other sharp objects, heating chemicals, recrystallizations, extractions, or centrifuging

Flammable or combustible substances

Flammable or combustible substances catch fire or burn in air. The process of burning requires:

- a combustible substance
- a supporter of combustion

- The vapors from a flammable liquid burns.
- Flash point of a liquid: Temp at which the liquid releases vapor in a sufficient amount to form an ignitable mixture with air near its surface.
- Liquids with flash points <100°F are generally termed flammable liquids
- Liquids with flash points of 100–200°F are called combustible liquids.
- Auto-ignition temperature is the temperature required to cause self-sustained combustion, independent of the source of heat.
- Vapor (with density >air) concentrates in lower areas can spread over a considerable distance, causing flash back to the source of the vapors

Pyrophoric substances

"Pyrophoric" if a small quantity of the material will ignite within 5 minutes after coming into contact with atmospheric oxygen. Spilling of pyrophoric material may cause a flash fire.

- Alkyl metals (e.g., t-butyllithium, trimethylaluminum, and diethylzinc)
- Alkyl metal halides (e.g., diethylaluminum bromide)
- Alkyl magnesium halides 'Grignard reagents' (e.g., methylmagnesium bromide)
- Alkylphosphines (e.g., triethylphosphine)
- Boranes (e.g., borane dimethylsulfide complex)
- White phosphorous
- Uranium IV oxide
- Super fine metal powders (e.g., iron, lead, nickel, platinum, aluminum)

Experience about Raney Nickel

Raney Ni is a common catalysis in green chemistry application, but please listen to the following story….

…I have had Raney Ni go up on me before. It's an exciting time when you have a fire in a Buchner funnel and all you are holding is a bottle of ethanol.

Weighing it out is easy because you buy it as a slurry in water.

The key is that when you filter the solids at the end of the reaction, never let the filter cake go dry. As long as there is a film of water/ethanol covering the metal surface it should be fine. ….

http://www.chemicalforums.com/index.php?topic=16289.0 on Raney Ni and not burning alive

Improper Handling of Unwanted Chemicals

University of Wisconsin April 2012

A researcher placed Pd/C into a plastic waste container in the lab. It was fortunate that a member of the custodial staff was near the lab when the fire started and was able to put the fire out before potentially spreading.

Many materials such as Raney Nickel, Pd/C, hydrides, and sodium and potassium used for chemical reactions still remain active after work-up. Pd/C is regularly used as a catalyst in hydrogenations and has been responsible for numerous accidents in academic labs nationwide. These catalysts require special handling and disposal procedures after manipulations, and cannot be simply placed in the trash.

www.ehs.wisc.edu/chem/HandlingUnwantedChemicals.pdf

Substances and mixtures emit flammable gases when in contact with water

- Category 1 – gases emitted ignite spontaneously or the rate of flammable gas evolution is ≥10 liters/kg of substance/minute
- Category 2 – rate of flammable gas evolution is ≥20 liters/kg of substance/hour
- Category 3 – rate of flammable gas evolution is ≥1 liter/kg of substance/hour

  - Alkali metals (e.g., lithium, sodium, etc.)
  - Metal hydrides (e.g., sodium hydride, lithium hydride, etc.)
  - Complex metal hydrides (e.g., lithium aluminum hydride, sodium aluminum hydride, etc.)
  - Calcium carbide

Substances and mixtures emit flammable gases when in contact with water

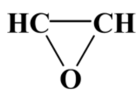
For example, the surface of a hot plate can ignite diethyl ether, which has an autoignition temperature (AIT) of 160°C (320°F).

The incident in Stanford 2013
http://web.stanford.edu/dept/EHS/prod/documents/13-235-1.pdf

- Reduction using LAH (5 g) in THF (100 mL)(FP -14 °C, AIT 321°C)
- **The remaining LAH (95 g) was placed next to the reaction apparatus**
- **Adjacent was an unrelated experiment involving pentane**
- Minutes after start of the reaction, the reaction flask over-pressurized causing the flask septum to pop off, initiating a fire in the hood.
- Initially used a CO_2 fire extinguisher spread the fire igniting the adjacent setup containing pentane.
- Next used Met-L-X®dry powder fire extinguishers to put out the hydride portion of the fire (FP -49 °C).
- Finally, a CO_2 extinguisher was used to extinguish the remaining other fuel sources..
- Several researchers reported smoke inhalation.

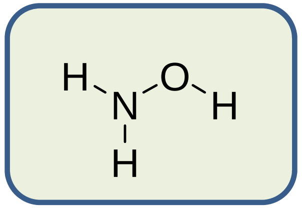
Explosives

Table 1. Atom Groupings that Indicate or Enhance Molecular Instability

Atom Grouping with Molecule	Example of Functional Group	
	Structure	Name
C-C and C-N triple bonds & their metal salts	-C≡C- ; -C≡N	Acetylenic; cyano
Adjacent N-O atoms - many combinations	C-NO_2 ; C-O-N=O	Aryl, alkyl nitro; alkyl nitrite
Adjacent and consecutive N atom pairs, triplets and higher	-C-N≡N ; -N-N≡N	Diazo; azide
Adjacent O-O pairs	-C-O-O-H ; C-O-O-C	Peroxyacids; peroxyesters, peroxides
Adjacent C atoms bridged by O or N and many ring combinations of 4 or less atoms	 	Epoxides, azetidine
O-X atomic pairs	-O-X ; -ClO_3	Hypohalites ; chlorates
Many N-Metal atomic pairs	=N-M	N – metal salts

D.J. Leggett, *Lab-HIRA: Hazard identification and risk analysis for the chemical research laboratory. Part 1. Preliminary Hazard Evaluation*, Journal of Chemical Health and Safety, 19, 9 – 24 (2012)

Decomposition of hydroxyamine



ΔH_{decomp} = 1.240 kcal/g (~TNT)

Potential hazards under the conditions

- conc > 50%
- heat
- oxidizing agents like $K_2Cr_2O_7$, CrO_3
- Zinc, Calcium, and Copper

A catastrophic hydroxylamine (HA) explosion during Feb 19, 1999, Concept Sciences, Inc. (CSI), Pennsylvania.
http://www.csb.gov/assets/1/19/Concept_case_study.pdf

Pressured gas cylinder system

Compressed gases present mechanical and chemical hazards.

• Flammable or combustible • Explosive • Corrosive • Poisonous • Inert

• or a combination of hazards

How to handle a gas cylinder

• Clearly identified the content, never rely on the color

• Gas lines should be clearly labeled

• Gas cylinders must be secured at all times to prevent tipping.

• Cylinder valves should be opened slowly

• Under no circumstances should any attempt be made to repair a cylinder or valve.

• The main cylinder valve should be closed as soon as it is no longer necessary that it be open, to prevent accident and to prevent the corrosion and contamination resulting from diffusion of air and moisture into the cylinder.

• A cylinder should never be emptied to a pressure lower than 172 kPa (25 psi/in2). The cylinder has to be clearly marked as "empty"

• The valve cap shall be replaced when moved

Oklahoma State University

Common mistakes on gas cylinder management

綠色化學講習會

中國化學會 2014年會

Common mistakes on gas cylinder management

Never left the cylinder unattended

http://www.chdist.com/images/products/70-118B_p.jpg
http://www.bremco.com.au/images/bmp078_gas_cylinder_trolley_single.jpg

Pressured gas cylinder system

… case report to show how devastating and fatal could be the pressure effect of oxygen gas. A 25 years man, a lorry driver …was rolling the cylinder keeping it slant with the pressure valve facing to his abdomen. All off a sudden the pressure valve came off and the compressed oxygen within the cylinder burst out through the outlet and hit his abdomen directly. He flew 20 feet far and died at the spot……

J Indian Acad Forensic Med. October-December 2013, Vol. 35, No. 4 392-397

gas cylinder.wmv

CO_2 Accident

Although CO2 has been used as a medium of supercritical fluid, CO2 can be very dangerous

Precautions that must be followed by those using or handling dry ice are:

• Do not put dry ice in a gas tight container. Excess pressure build up can cause containers to explode!

• Do not store dry ice in cold rooms or any other unventilated room

Properties

• Asphyxiant: in high concentrations sublimed vapour may cause asphyxiation. Expansion ratio (relative increase in volume when evaporating to gas) for dry ice is 845; 10 kg of dry ice sublimes into about 5.4 m^3 of carbon dioxide gas

• Extremely cold: having a product temperature of -78°C dry ice is a good source of extreme cold but contact with the product can cause cold burns or frostbite.

CO_2 Accident

CO_2 Evaculation

A Siloam Springs plant was evacuated Saturday morning (Aug. 31) after an accident involving dry ice caused a carbon dioxide gas cloud, simply because dry ice came in contact with the water. ….“When our crew arrived, which was four minutes later, we had multiple patients, and so we knew we had something larger,” Siloam Springs Fire Chief Greg Neely said. “There was coughing, shortness of breath and just an overall sense of urgency about them. When you can’t breathe, that’s very alarming.”… Dry Ice Accident Forces Evacuation, Sends 34 to Hospital

POSTED 1:15 PM, AUGUST 31, 2013, BY MARTY COOK AND KATIE KORMANN, *UPDATED AT 10:26PM, AUGUST 31, 2013* http://5newsonline.com/2013/08/31/dry-ice-accident-forces-evacuation-sends-34-to-hospital/

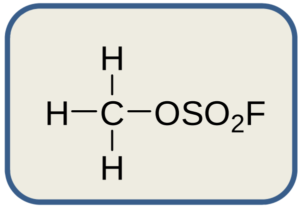
A story of CO_2 Bomb

…. as it was approaching 5 - and there was no real rush on this experiment. She figured she might as well just clean up and go home. So... Washed the glass, put away all reagents, scrubbed up, but didn’t want to waste the 10 lbs of good dry ice. Sooooo... She figured it wouldn’t melt away in the fridge! Better yet, there was a really cold one with a locking door. Sometime during the night, the pressure built, and the door was blown 30 feet away in the lab next door - through the cinder block wall, leaving a 3 foot wide, 8 foot tall hole. Thank god no one was around. …..

http://chemistry.about.com/u/ua/healthsafety/labaccidents.htm

CO2 bomb.wmv

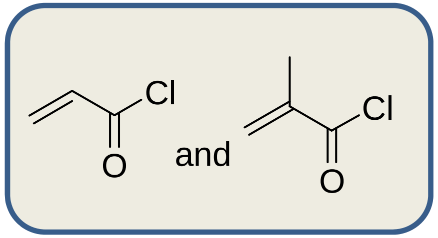
Other fatal examples on chemical spills



March 25, 1976 Tech Univ Twente, Netherlands Methylfluorosulphate (CH_3OSO_2F) is a common methylating agent. At 11.30 A.M. a 25-year-old chemist spilt a few millilitres of a fluid containing CH_3OSO_2F on his laboratory coat and pullover. He immediately took off the coat and cleaned his pullover with water.

- No abnormality was found.
- At 5 P.M. the man began to cough a little and had some difficulty with deep breathing.
- At 7 P.M. he was admitted to hospital in a moribund state due to pulmonary cedema. He died the next day despite intensive treatment.
- Protein denaturation seems to be the major contributor to the development of pulmonary oedema.

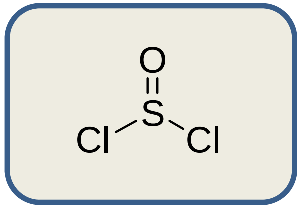
J Admiraal, The Lancet, 1976, 854



Acryloyl chloride and methacryloyl chloride were overtuned. The student stay briefly in the lab to rinse his irritated eyes and arrived at the hospital 1 h later. He developed progressive shortness of breath 6 h after admission and died 23 h after admission due to pulmonary oedema

FL Lau, SYChu, TS Yu European Journal of Emergency Medicin
1998, 5 265-257

Other fatal examples on chemical spills



Hee Yeon Cho, a Boston College graduate student reportedly suffered minor injuries

- Cho was working with thionyl chloride, $SOCl_2$ (current Sigma Aldrich MSDS available here). Thionyl chloride is toxic and reacts violently with water, bases, some metals, and a few other things
- Cho was, however, working alone.
- When her experiment blew up, she left the lab to go home and tend to her injuries.
- Cho's injuries were reportedly minor–cuts on her face and burns on her hands.

http://cenblog.org/the-safety-zone/2011/06/boston-college-student-injured-in-lab-explosion/ Jyllian Kemsley C&EN The safety zone

Summary

- Research lab of green chemistry may not be safe
- Creating and understanding safety culture is important
- Safety education has to be broad-based, only small group of professional people understanding safety issues is not enough to secure safety
- Chemical intuition about chemical structure reactivity and chemical hazards are important

•References for Chemical Safety

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- (2) Safety in Academic Chemistry Laboratory Vol 2. 7 Ed Accident prevention for faculty and administrators and university students, ACS **2003**
- (3) Chemical Safety Manual for Small Businesses 3 Ed, ACS **2007**
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- (5) Handbook of Chemical Health and Safety, Edited by Robert J. Alaimo American Chemical Society **2001**
- (6) A Comprehensive Guide to the Hazardous Properties of Chemical Substances. 3 rd ED. ACS, P. Patnaik American Chemical Society **2007**
- (7) Prudent Practices in the Laboratory Handling and Disposal of Chemicals National Research Council **1995**
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- (10) Wiley Guide to Chemical Incompatibilities 2 ed, R. J. Pohanish, S. A. Greene , Wiley, **2006**
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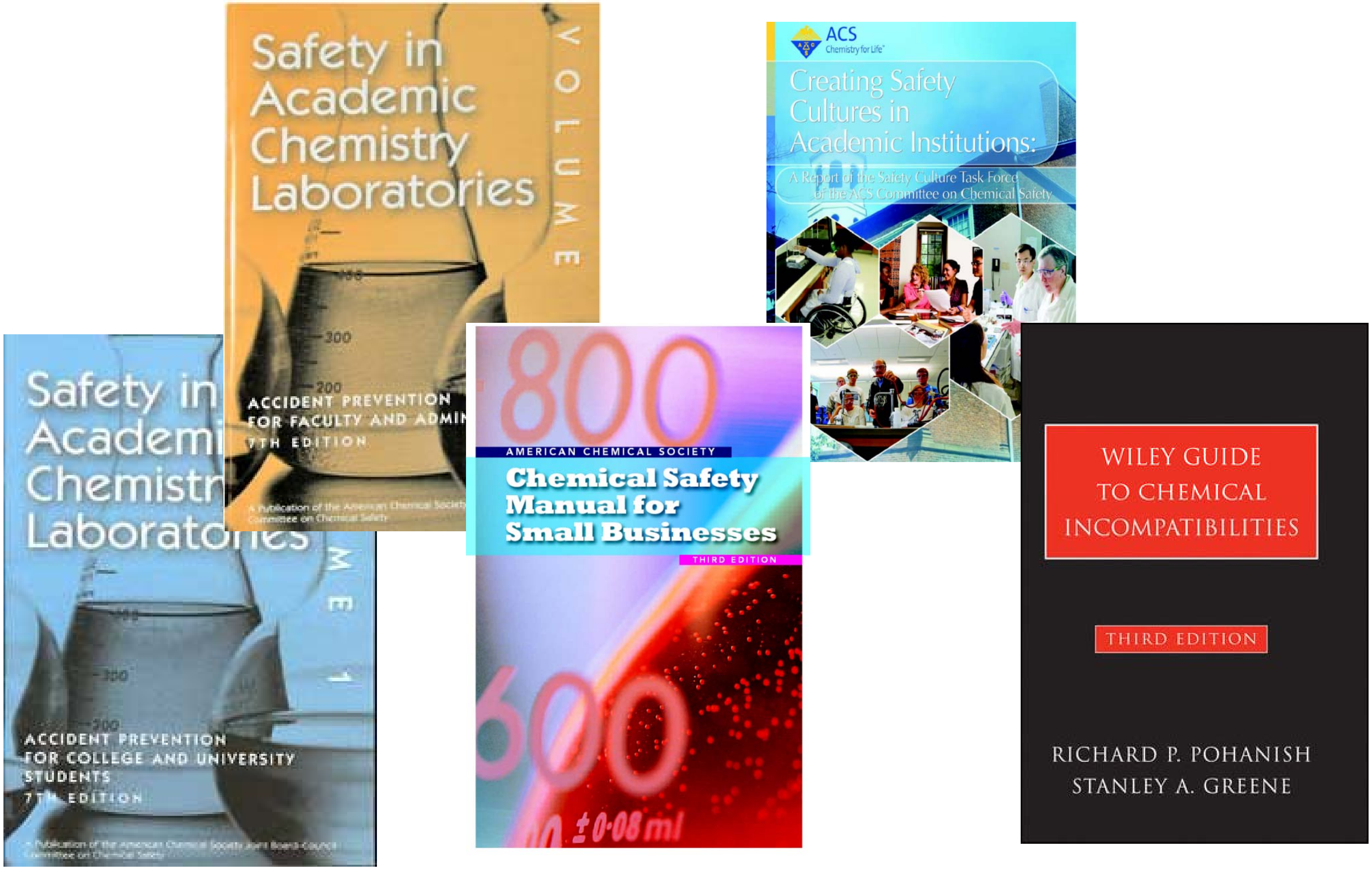
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ACCIDENT PREVENTION FOR COLLEGE AND UNIVERSITY STUDENTS
7TH EDITION
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Creating Safety Cultures in Academic Institutions:
A Report of the Safety Culture Task Force of the ACS Committee on Chemical Safety
800
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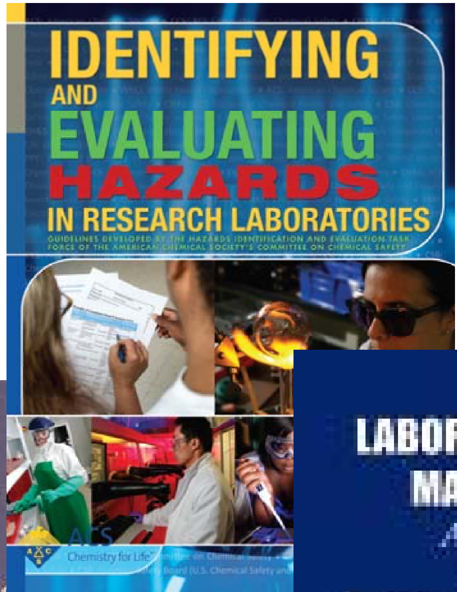
Chemical Safety Manual for Small Businesses
THIRD EDITION
600
WILEY GUIDE TO CHEMICAL INCOMPATIBILITIES
THIRD EDITION
RICHARD P. POHANISH
STANLEY A. GREENE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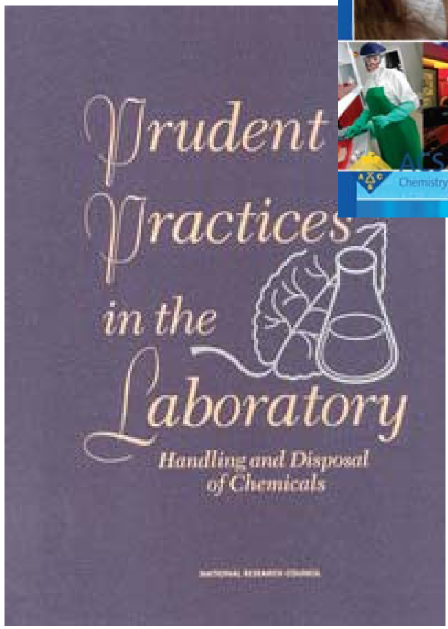
AND
EVALUATING
HAZARDS
IN RESEARCH LABORATORIES


HANDBOOK OF
CHEMICAL HEALTH AND SAFETY
ROBERT J. ALAIMO
Editor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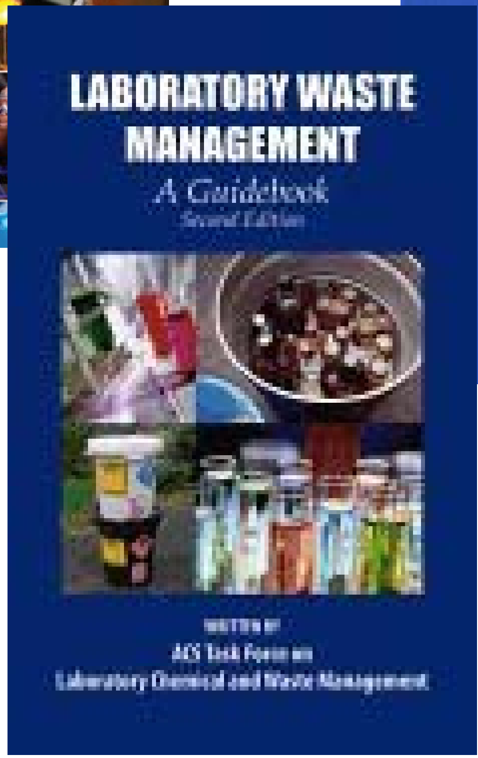
of Chemicals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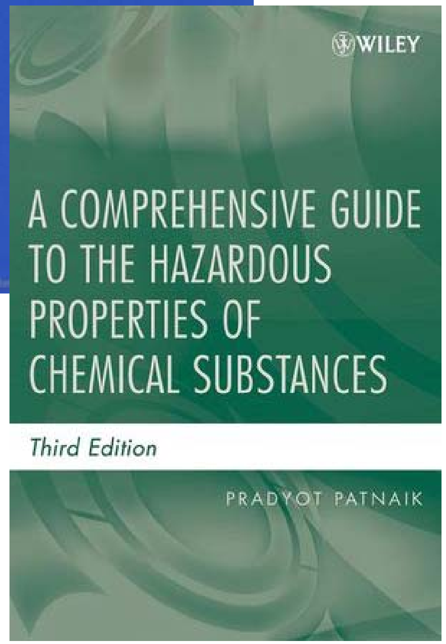
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Frostbite Injury of Hand Caused by Liquid Helium: A Case Report

Celalettin Sever, MD, Yalcin Kulahci, MD, Ali Acar, MD, and Haluk Duman, MDa Open access journal of plastic surgery 2010, 287
http://www.ncbi.nlm.nih.gov/pmc/articles/PMC2873703/

Evaporated Liquid Nitrogen-Induced Asphyxia: A Case Report

A 27-yr-old postgraduate student was found lying in a right lateral decubitis position on the latticed plastic pallets paving the floor of an underground dry area adjacent to a research building, approximately 12:00 p.m. on a day in June. The primary cause of death was asphyxia by evaporated liquid nitrogen.

Kim, Dong-Hoon; Lee, Hyung-Jong
J Korean Med Sci 2008; 23: 163-5

A college officer mentioned that the LN2 cylinder was fully filled on the day before the accident.

74

Cryogenic burn by liquid nitrogen

week 1

week 2

week 3

http://asktheburnsurgeon.blogspot.tw/2012_03_25_archive.html