Institute of
Organic Chemistry
NAS of Ukraine

LABORATORY SAFETY TRAINING

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OBJECTIVES

At the end of the discussion, the students must be able to:

- Discuss safety awareness for laboratory personnel.
- Identify hazards related to handling chemicals.
- Choose appropriate personal protective equipment when working in the laboratory.
- Identify the classes of fires and the type of fire extinguishers to use for each.
- Describe steps used as precautionary measures when working with electrical equipment, cryogenic materials, and compressed gases and avoiding mechanical hazards associated with laboratory equipment.
- Select correct means for disposal of waste generated in the laboratory.

Regulations

International

Occupational Safety and Health Administration

OSHA®

Occupational Safety and Health Administration

OSHA

OSHA officially formed on April 28, 1971, USA

Ukraine

МІНІСТЕРСТВО НАДЗВИЧАЙНИХ СИТУАЦІЙ УКРАЇНИ
НАКАЗ

11.09.2012 № 1192

Зареєстровано в Міністерстві юстиції України
25 вересня 2012 р.
за № 1648/21960

Про затвердження Правил охорони праці під час роботи в хімічних лабораторіях

USA Statistics (9 States) (1999-2008)

There were **57,975** incidents involving hazardous chemical substances and **4,621** of those incidents resulted in **15,506** persons being injured. More than 1/3 of injuries occurred in the Top 5 Industries and 30% of the incidents occurred in those industries. The Chemical Manufacturing (CM) industry was #1 with 1,753 persons injured, but surprisingly Educational Services (ES) was ranked #2 with 1,562 persons injured. Human error was the leading contributing factor in these injuries for ES, followed by intentional or illegal acts, and then equipment failures. For CS there were **407** student injuries (23% of 1,753 injuries) and for ES there were **1,092** student injuries (70% of 1,562 injuries).

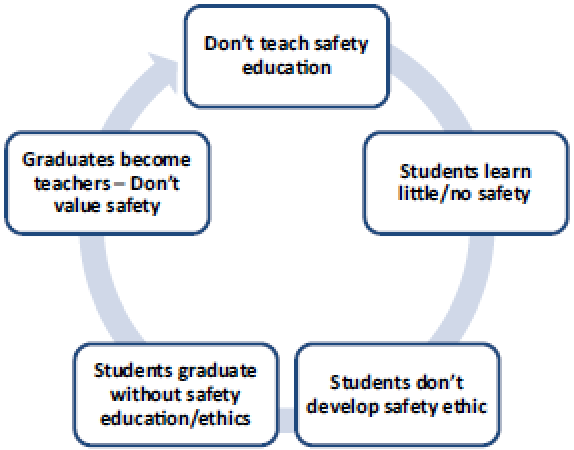


Figure 1. Today's cycle in academia that does not teach safety, thus bringing new graduates through a process that does not value safety.

Journal of Chemical Health & Safety, 2015, dx.doi.org/10.1016/j.jchas.2015.10.017

RAMP

- **R**ecognize hazards
- **A**ssess the risks of hazards
- **M**inimize the risks of hazards
- **P**repare for emergencies

Hill, R. H.; Finster, D. C. Laboratory Safety for Chemistry Students; John Wiley & Sons, Inc.: Hoboken, NJ, 2010.

Hazard versus Risk

Examples of Hazards and Their Effects

Type of Hazard	Example	Potential Harm
Item	Broken glass	Cut
Substance	Sodium hydroxide	Blistering of skin
Source of energy	Bunsen burner	Burn
Condition	Wet floor	Slipping and falling

POTENTIAL HAZARDS

1. Electric shock
2. Toxic vapors & irritants
3. Compressed gases
4. Flammable liquids
5. Corrosive substances
6. Mechanical trauma
7. Poisons
8. Cryogenic materials

LABORATORY SAFETY

Safety begins with recognition of hazards and is achieved through the application of:

- ✓ Common sense.
- ✓ A safety-focused attitude.
- ✓ Good personal behavior/habits.
- ✓ Good housekeeping.
- ✓ Continual practice of good laboratory technique.

Good personal behavior/habits

- ✓Wear proper attire and protective clothing
- ✓Tie back long hair
- ✓Do not eat, drink, or smoke in the work area
- ✓Never mouth pipet
- ✓Wash hands frequently

Good housekeeping

- ✓ Keep work areas free of chemicals, dirty glassware, etc.
- ✓ Store chemicals properly
- ✓ Label reagents and solutions
- ✓ Post warning sings

Continual practice of good laboratory technique

- ✓ Don’t operate new or unfamiliar equipment until you have received instruction and authorization
- ✓ Read all labels and instructions carefully
- ✓ Use the PPE that is provided
- ✓ For the safe handling, uses, and disposal of chemicals, learn their properties and hazards.
- ✓ Learn emergency procedures and become familiar with the location of fire exits, fire extinguishers, blankets, etc.
- ✓ Be careful when transferring chemicals from container to container and always add acid to water slowly.

In most cases, accidents can be traced directly to two primary causes:

1. Unsafe acts (PERSONAL)
2. Unsafe conditions (ENVIRONMENTAL)

3 Strategies to contain hazards:

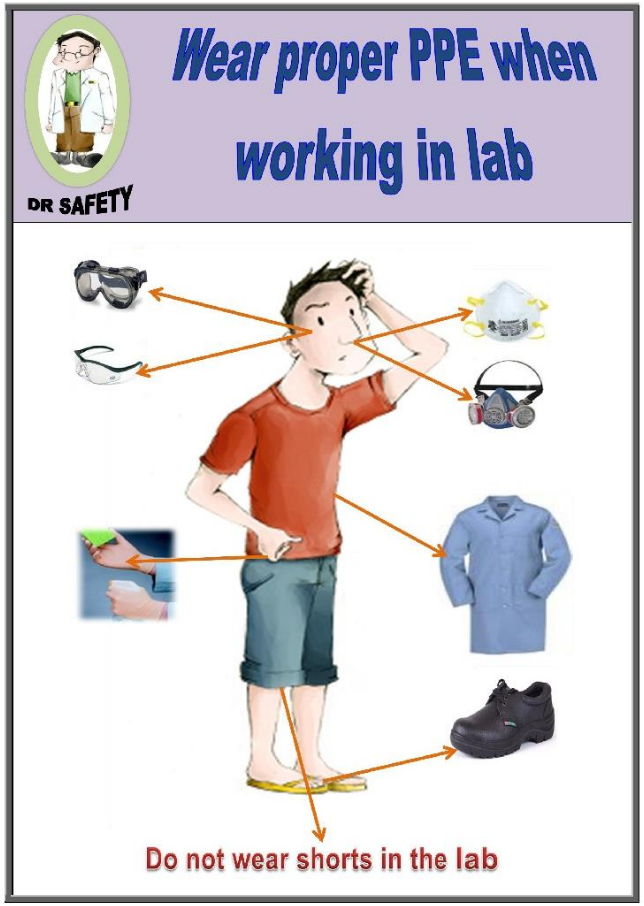
1. Engineering Controls
2. Personal Protective Equipment
3. Work Practice Controls

Engineering Controls

Engineering controls are safety features built into the overall design of a product

- ✓ Circuit breakers
- ✓ Puncture resistant containers for disposal
- ✓ Splash guards
- ✓ Volatile liquid containers
- ✓ Centrifuge safety buckets
- ✓ fume hoods
- ✓ Mechanical pipetting devices
- ✓ Sensor/foot controlled sinks and faucets

LABORATORY SAFETY



Personal protective equipment and barriers like gloves and face shields physically separate the user from a hazard.

Personal
Protective
Equipment
(PPE)

Personal Protective Equipment



Eye Protection


Nobel Laureate K. Barry Sharpless accident, 1970

A cautionary tale from the past

Many of you may know that **I was blinded in one eye during a lab accident in 1970**, shortly after I arrived at MIT as an assistant professor. I always wore glasses whenever I was at my bench, and while I felt I conscientiously observed safety measures, my experience proves one can't be too cautious about wearing safety glasses. As I prepared to go home from the lab during the early hours of the morning of the accident, I looked in the bays to see what my co-workers were doing, and then returned to my own bench, removed my safety glasses, and put on my parka. As I was walking to the door, I passed the bench where a first-year graduate student was flame-sealing an NMR tube. I asked how it was going, and he replied, "Good, I've got it sealed."

I stopped by his bench, picked up the tube from the bath, and held it to the light. The tube immediately frosted over, and, as I wiped it to better see the contents, I noticed that the solvent level was exceedingly high. Suddenly the solvent level dropped several inches. Though I instantly realized condensed oxygen had been sealed in the NMR tube, I was quite literally unable to move a muscle before it exploded. Glass fragments shredded my cornea, penetrated the iris, and cause the partial collapse of one eye. My only other injuries were superficial face cuts.

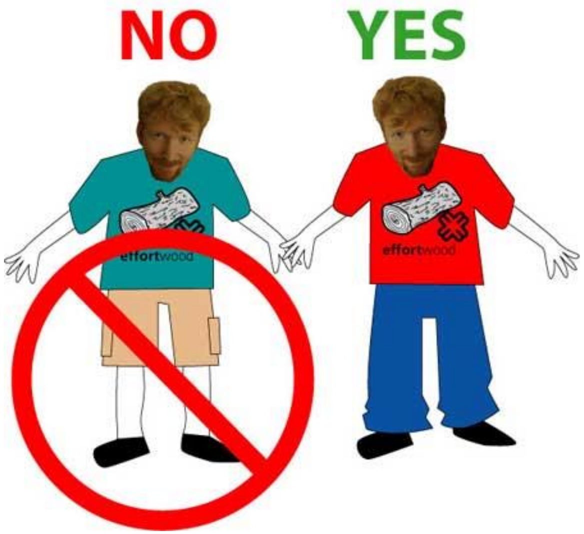
K. Barry Sharpless, | Professor March 11, 1992 MIT Tech Talk (Vol. 36, # 23)

Personal Protective Equipment

Gloves

Personal Protective Equipment

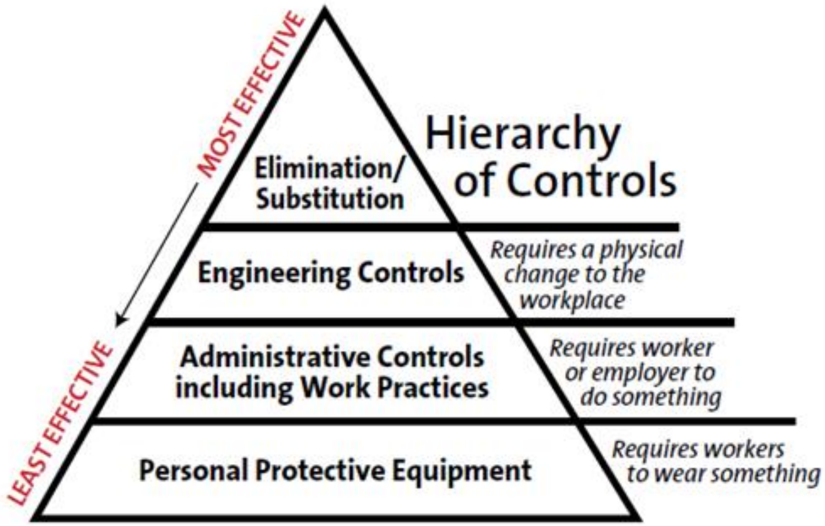
Clothing



Work practice controls include general procedures and preventive measures that reduce or eliminate exposure to hazards

- ✓ Hand washing
- ✓ Cleaning surfaces
- ✓ Avoiding unnecessary use
- ✓ Red bag waste disposal
- ✓ Orientation, training, and continuing education
- ✓ No eating, drinking, or smoking
- ✓ Warning signage

LABORATORY SAFETY



***Elimination**: the initial design of the facility, equipment, chemicals, or process to remove hazards.*

***Substitution**: using a less hazardous substance or process; selecting another solvent that allows for lower reaction temperature or pressure, less toxic reactants, etc.*

***Engineering**: laboratory hoods, gloveboxes, biosafety cabinets, snorkels, safety interlocks, lead shielding, inert atmospheres, etc.*

***Administrative**: implementation of procedures and policies (standard operating procedures), training, reducing exposure times, attention to nearby employees or other students, signage, best work practices, not working alone, etc.*

SAFETY PRACTICES

General Practices:

1. Smoking, eating, and application of cosmetics are prohibited.
2. Protective garment must be worn over clothing.
3. Shoes should be made of nonporous material with closed toes and heels.
4. Contact lenses should be discouraged.
5. Goggles or face shields are recommended if contact lenses are worn.
6. Dangling jewelry, long hair, and beards are not allowed.
7. Mouth pipetting should be strictly prohibited.

Labels and Signage:

- ✓ All chemical containers should be clearly labelled.
- ✓ Appropriate **signs to identify hazards** are critical.
- ✓ Areas where flammables, hazardous or toxic chemicals, and carcinogens are stored or being used must be clearly marked.

SAFETY PRACTICES

Flammable

Harmful / Irritant

Corrosive

Poison / Toxic

Explosion

Biohazard

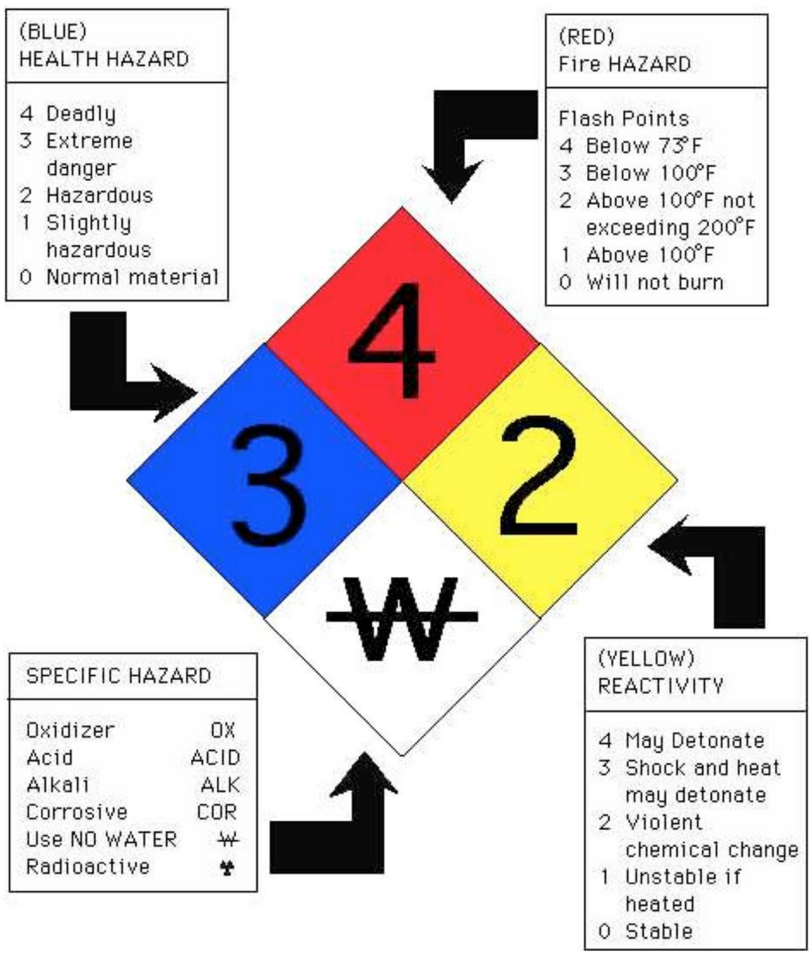
Oxidizer

Environmental Hazard

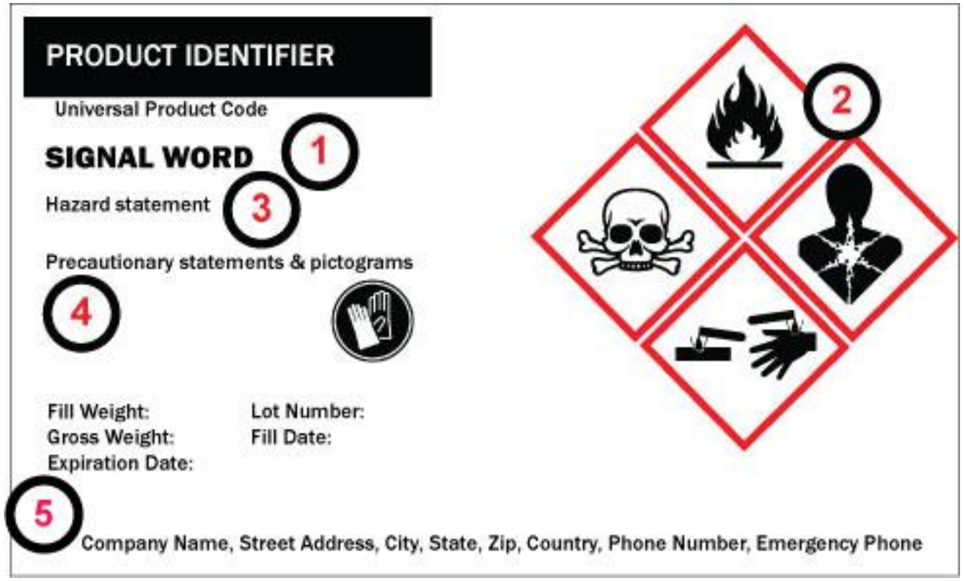
Radioactive

SAFETY PRACTICES

NFPA

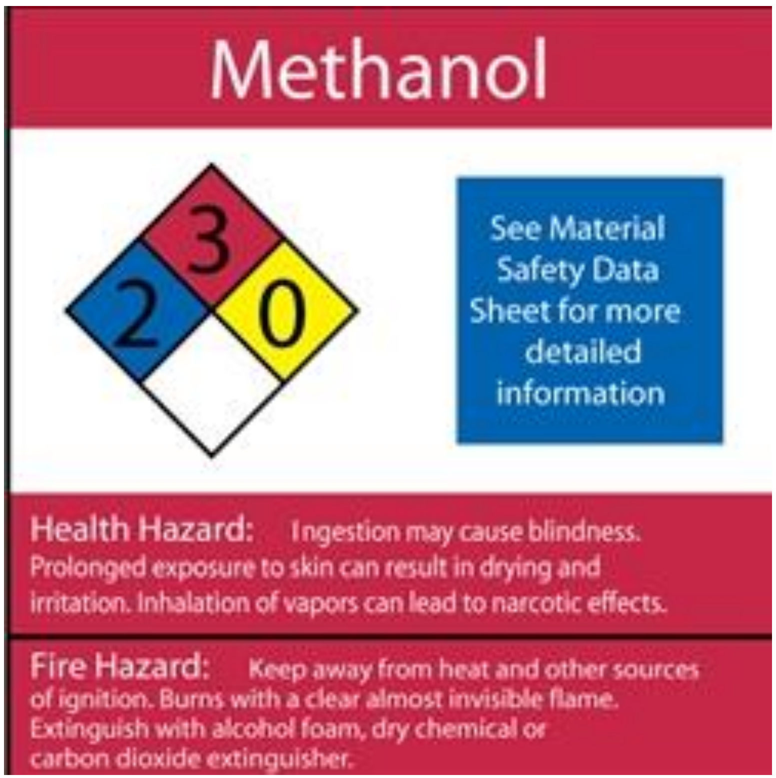


Globally Harmonized System (GHS)

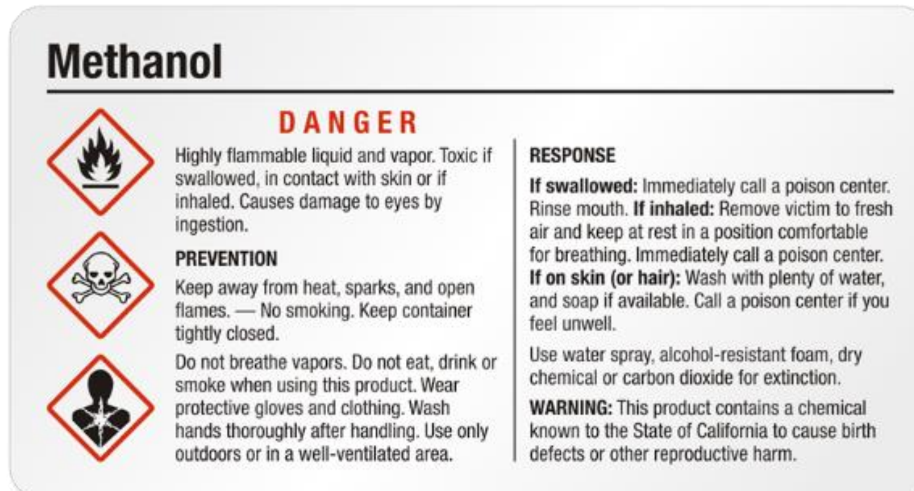


SAFETY PRACTICES

NFPA



GHS



SAFETY EQUIPMENT

1. Hoods
   - Fume Hoods
2. Chemical storage equipment
3. Personal protective equipment (PPE)

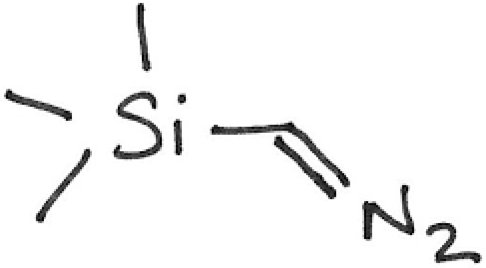
HOODS

Fume Hoods

- ✓ Fume hoods are used when chemical reagents may produce a hazardous fume.
- ✓ The sash or window should be lowered when working in the hood.
- ✓ Air flow should be checked to assure proper ventilation.
- ✓ Controls such as power, gas, and vacuum should be located externally to prevent a spark that may cause a fire when using volatiles.

Ronald Daigle accident, Oct. 8, 2008, Sepracor Canada , Windsor, Nova Scotia

Daigle died on Oct. 8, 2008, from lung failure after exposure to **trimethylsilyldiazomethane (TMSD)** in a quality control laboratory



The day before he died, Daigle, 46, worked with TMSD, $(CH_3)_3SiCHN_2$, when lab fume hoods were not operating because of roof work. TMSD can be used as a methylating reagent in place of diazomethane, which is explosive. When inhaled, diazomethane can also cause fatal lung damage akin to that experienced by Daigle.

The company agreed to a deal that involved pleading guilty to one charge of failing to provide proper workplace ventilation and a $47,000 fine.

Chemical & Engineering News, *2011, 89, #19, p. 15*

SAFETY EQUIPMENT

CHEMICAL STORAGE EQUIPMENT

- ✓ Safety equipment is available for the storage and handling of chemicals and compressed gases.
- ✓ Safety carriers should always be used to transport 500-mL bottles of acids, alkalis, or other solvents, and approved safety cans should be used for storing, dispensing, or disposing of flammables in volumes greater than 1 qt.

PERSONAL PROTECTIVE EQUIPMENT (PPE)

- ✓ The parts of the body most frequently subject to injury in the clinical laboratory are the ***eyes, skin, and respiratory and digestive tracts***. Hence, the use of personal protective equipment is very important.
- ✓ All contaminated PPE must be removed and properly disposed of before leaving the laboratory.

CHEMICAL SAFETY

Hazard Communication

- ✓ Students must be informed of the health risks associated with those chemicals.
- ✓ This ensures that health hazards are evaluated for all chemicals that are produced and that this information is relayed to students.

To comply with the new Hazard Communication Standard, laboratories must:

- ✓ Plan and implement a written hazard communication program.
- ✓ Obtain ***material safety data sheets*** **(MSDS)** for each hazardous compound present in the workplace and have the MSDS readily accessible to employees.
- ✓ Educate all employees annually on how to interpret chemical labels, MSDS, and health hazards of the chemicals and how to work safely with the chemicals.
- ✓ Maintain hazard warning labels on containers received or filled on site.

Chemical Hygiene Plan (CHP)

The written CHP must include the following:

1. Criteria for and methods of monitoring chemical exposure
2. Standard operating procedures for handling hazardous chemicals
3. Criteria for implementing engineering controls (fume hoods)
4. Use of personal protective equipment and other hygiene practices
5. Special precautions for extremely hazardous chemicals

Chemical Hygiene Plan (CHP)

The written CHP must include the following:

6. Specific measures to ensure that fume hoods and other equipment are working properly
7. Provision for employee information and training
8. Provision for medical consultation and examination
9. Designation of a chemical hygiene officer responsible for implementation of the CHP.

Categories of Chemicals:

- ✓ Since the laboratory deals with a wide variety of chemicals, clinical laboratory scientists must understand the potential hazards involved in their use.
- ✓ Chemicals may have **health hazards** or **physical hazards.**

Material Safety Data Sheet

- ✓ The MSDS is a major source of safety information for employees who may use *hazardous materials* in their occupations.
- ✓ Employers are responsible for obtaining from the chemical manufacturer or developing an MSDS for each hazardous agent used in the workplace.
- ✓ A standardized format is not mandatory, but all requirements listed in the law must be addressed.

Material Safety Data Sheet

Information contained on a material safety data sheet includes the following:

- Product name and identification
- Hazardous ingredients
- Permissible Exposure Limit (PEL)
- Physical and chemical data
- Health hazard data and carcinogenic potential
- Primary routes of entry
- Fire and exposure hazards
- Reactivity data
- Spill and disposal procedures
- Personal protective equipment recommendations
- Handling
- Emergency and first aid procedures
- Storage and transportation precautions
- Chemical manufacturer’s name, address, and phone number
- Special information section

SIGMA-ALDRICH

sigma-aldrich.com

Material Safety Data Sheet

Version 6.0
Revision Date 02/08/2013
Print Date 11/25/2013

1. PRODUCT AND COMPANY IDENTIFICATION

Product name	:	Methanol
Product Number	:	322415
Brand	:	Sigma-Aldrich
Supplier	:	Sigma-Aldrich 3050 Spruce Street SAINT LOUIS MO 63103 USA
Telephone	:	+1 800-325-5832
Fax	:	+1 800-325-5052
Emergency Phone # (For both supplier and manufacturer)	:	(314) 776-6555
Preparation Information	:	Sigma-Aldrich Corporation Product Safety - Americas Region 1-800-521-8956

2. HAZARDS IDENTIFICATION

Emergency Overview

OSHA Hazards
Flammable liquid, Target Organ Effect, Toxic by inhalation., Toxic by ingestion, Toxic by skin absorption

Target Organs

Eyes, Kidney, Liver, Heart, Central nervous system

GHS Classification
Flammable liquids (Category 2)
Acute toxicity, Oral (Category 3)
Acute toxicity, Inhalation (Category 3)
Acute toxicity, Dermal (Category 3)
Specific target organ toxicity - single exposure (Category 1)

GHS Label elements, including precautionary statements

Pictogram 

Signal word Danger

Hazard statement(s)

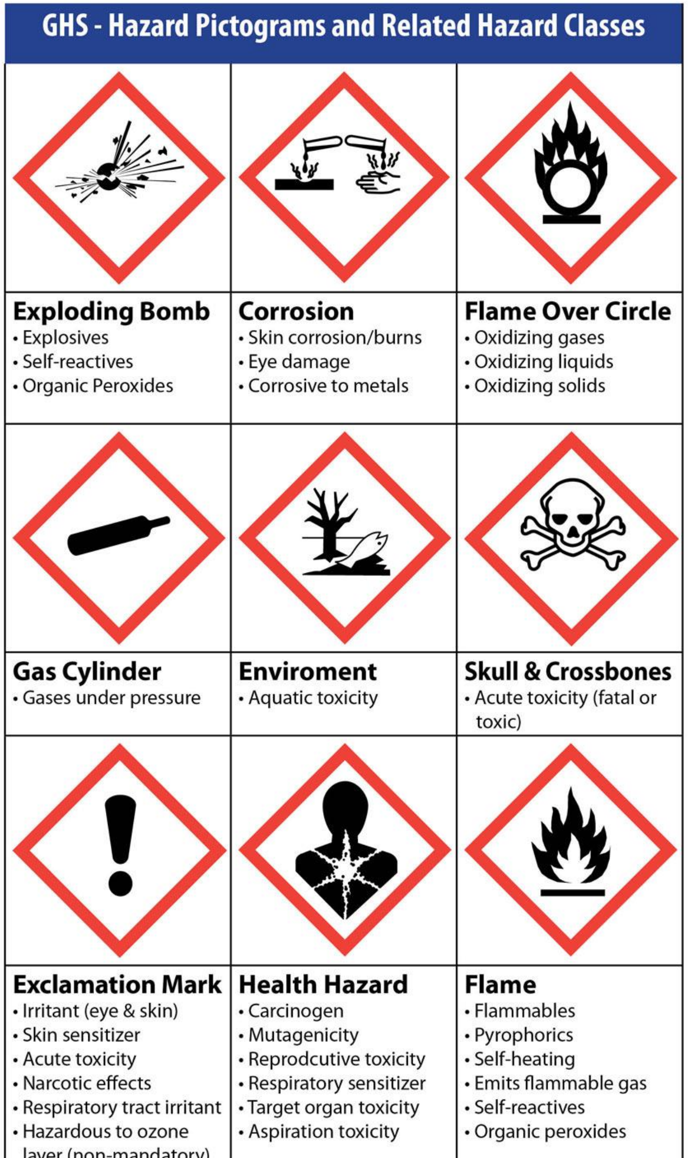
H225	Highly flammable liquid and vapour.
H301 + H311 + H331	Toxic if swallowed, in contact with skin or if inhaled
H370	Causes damage to organs.

Precautionary statement(s)

P210	Keep away from heat/sparks/open flames/hot surfaces. - No smoking.
P260	Do not breathe dust/ fume/ gas/ mist/ vapours/ spray.
P280	Wear protective gloves/ protective clothing.
P301 + P310	IF SWALLOWED: Immediately call a POISON CENTER or doctor/ physician.
P307 + P311	IF exposed: Call a POISON CENTER or doctor/ physician.

HMIS Classification
Health hazard: 2

CHEMICAL SAFETY



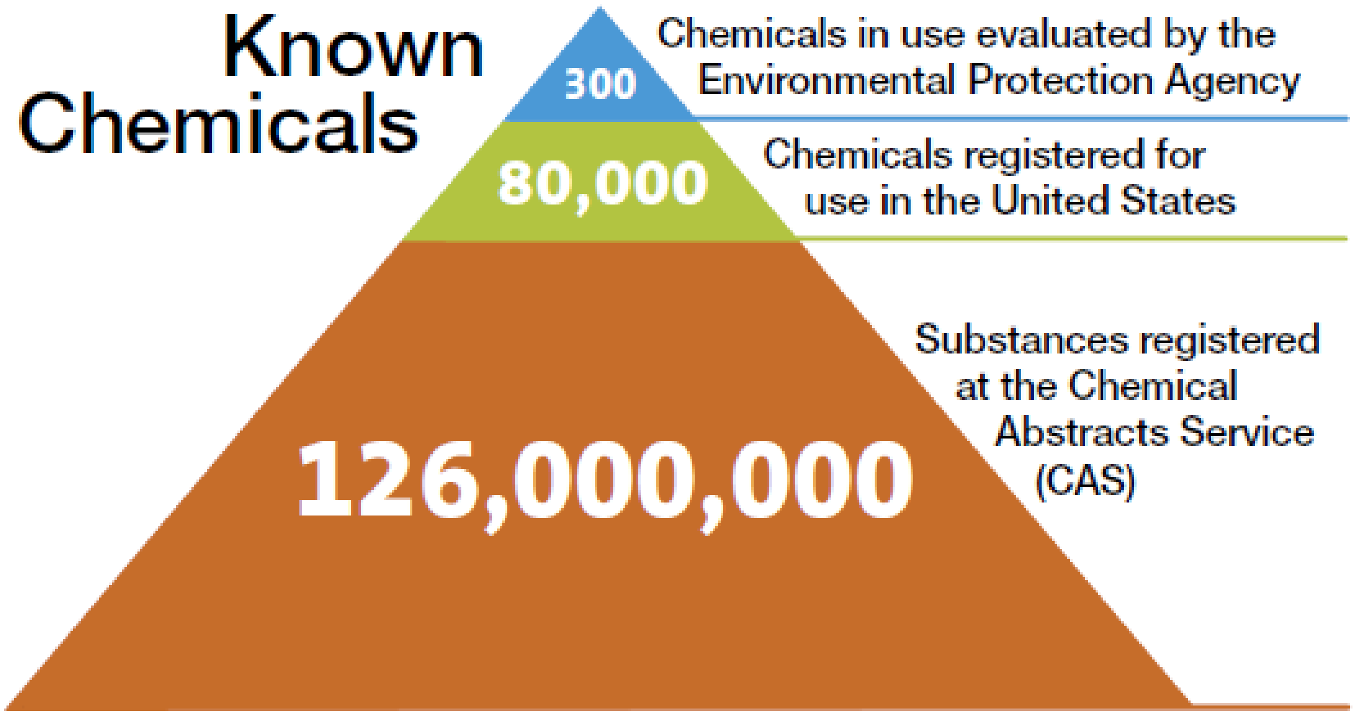
- Product Identifier
- Pictogram(s)
- Signal Word

  Danger or Warning
- Hazard Statement(s)

  Standardized and assigned phrases that describe the hazard(s) as determined by hazard Classification.
- Precautionary Statement(s)

  Supplements the hazard information by briefly providing measures to be taken to minimize or prevent adverse effects from physical, health or environmental hazards. First aid is included in precautionary information.

CHEMICAL SAFETY



Categories of Chemicals

1. ***Corrosives*** – chemicals with a pH of ≤ 2 or ≥ 12.5.
2. ***Toxic substances*** – poisons, irritants, asphyxiants
3. ***Carcinogens*** – capable of causing cancer.
4. ***Mutagens and teratogens*** – capable of causing chromosomal aberrations or congenital malformations.
5. ***Ignitable*** – flammables and combustibles.
6. ***Reactive*** – explosive and oxidizers.

CORROSIVE CHEMICALS

- ✓ Corrosive chemicals are injurious to the skin or eyes by direct contact or to the tissue of the respiratory and gastrointestinal tracts if inhaled or ingested.
- ✓ Commonly used corrosives in the laboratory:
  - **Concentrated acids** – such as hydrochloric, nitric, sulfuric, and acetic
  - **Concentrated alkalis** – sodium hydroxide, potassium hydroxide, and ammonium hydroxide.

TOXIC SUBSTANCES

- ✓ Toxic substances include **poisons**, **irritants**, **and asphyxiants.**
- ✓ They do not act directly with human tissue but interfere with the metabolic processes of the body.
- ✓ They may enter the body by:
  1. Ingestion
  2. Inhalation
  3. Injection
  4. Skin absorption

Bhopal Gas Disaster

- ✓ The Union Carbide Pesticide Plant in Bhopal, released 40 tons of Methyl Isocyanate (MIC) gas, killing between 2,500 to 5,000 people in the early hours of the morning.
- ✓ The World's worst Industrial Disaster

Bhopal Gas Disaster

- The gas being heavier than air, started entering into the homes of the unwary population. Many who panicked and ran out also got crushed in stampedes.
- Around 500,000 were estimated to be exposed to the gas & around 20,000 have died as a result. Over 120,000 continue to suffer from the from the effects of the disaster.

Viktor Yushchenko was poisoned by DIOXINE, LD_{50} = 0.2 mg/kg (Before and After)

Published online 23 November 2004 | Nature | doi:10.1038/news041122-8

CHEMICAL SAFETY

TOXIC SUBSTANCES:

- Cyanides
- Cadmium
- Mercury
- Osmium
- Acrylamide
- Ethidium Bromide
- Sodium Azide

Poisonous Compressed Gases

- Carbon Monoxide
- Hydrogen Sulfide
- Hydrogen Chloride

3 types of damage caused by a toxic chemical:

- ✓Damage to biological structure
- ✓Disturbance of biological function
- ✓Damaging **both** structure and function

Damage……

Local - affects only the exposed part.

Contact through absorption, inhalation, ingestion, or injection

Systemic - effect of a substance after absorption the bloodstream.

Absorption may take place through the skin, stomach, or lungs.

Acute or Chronic damage?

✓**Acute toxicity** - victim becomes ill or injured after "short exposure" sometimes just a few moments

✓**Chronic toxicity** - effects of a toxicant on a body over a long period, sometimes several years

Effects may not be noticed until the damage is too far advanced to correct.

Variables Affecting Toxicity

Not everyone suffers equally from toxicity. The effects may vary from person to person depending on:

- ✓ Mode of entry
- ✓ Physical Condition
- ✓ Dose and/or Duration
- ✓ Sensitivity; Stress
- ✓ Combined effects
- ✓ Gender, race, temperature, altitude, body chemistry

Measuring Toxicity: TLV

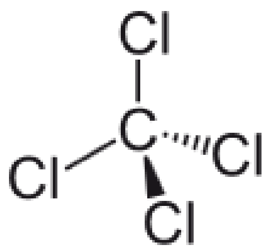
- ✓ Threshold Limit Value
- ✓ The maximum concentration of a toxicant or corrosive in air that is known NOT to cause damage or illness.
- ✓ Units are ppm (parts per million)
- ✓ Used to describe toxicity by inhalation

TOXIC SUBSTANCES

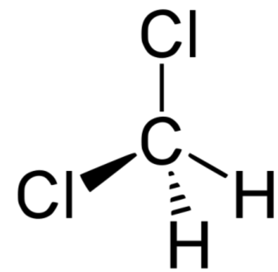
There are three different TLVs:

1. **Time-weighted average (TLV-TWA)** – represents the maximum allowable exposure over an 8-hour work day.
2. **Short-term exposure limit (TLV-STEL)** – represents the maximum amount of allowable exposure for a short period such as 15 minutes. (can’t be repeated more than 4 times per day)
3. **Ceiling value form (TLV-C)** – represents the concentration of an agent that must never be exceeded.

CHEMICAL SAFETY



Tetrachloromethane
(Carbon Tetrachloride)



Dichloromethane
(Methylene Chloride)

GHS Label elements, including precautionary statements

Pictogram	
Signal word	Danger
Hazard statement(s) H301 + H311 + H331	Toxic if swallowed, in contact with skin or if inhaled

GHS Label elements, including precautionary statements

Pictogram	
Signal word	Warning
Hazard statement(s) H303 + H313	May be harmful if swallowed or in contact with skin.

TWA	5 ppm	TWA	50 ppm
STEL	10 ppm	STEL	125 ppm

Measuring Toxicity: LD_{50}
The Median Lethal Dose

- ✓ Lethal Dose. 50% kill
- ✓ The dose which, when administered to test animals, kills half of them.
- ✓ Usually refers to ingestion or injection
- ✓ Units are mg of toxicant per kg of body mass
- ✓ Correlating rat-doses to man-doses
- ✓ LD50 for a chemical ingested by rats is 8 mg/kg. How much would each person in a group of 150 lb people need to ingest to have a 50% fatality rate?

Measuring Toxicity: LC_{50}
The Median Lethal Concentration

- ✓ The concentration of a chemical in an environment (generally air or water) which produces death in 50% of an exposed population of test animals in a specified time frame
- ✓ Normally expressed as milligrams of substance per liter of air or water (or as ppm)

CHEMICAL SAFETY

Toxicity rating	Example	LD_{50} (mg/kg)
Slightly toxic (5-15 g/kg)	Ethanol	8000
Moderately toxic (0.5-5 g/kg)	Sodium chloride Parathion	4000 1300
Very toxic (50-500 mg/kg)	Aspirin Paracetamol	300 300
Extremely toxic (5-50 mg/kg)	Theophylline Diphenhydramine	50 25
Super Toxic (<5 mg/kg)	Potassium cynanide Digoxin Tetrodotoxin Botulinum toxin	3 0.2 0.01 0.00001 (10 ng/kg !)


ACUTE ORAL TOXICITY – Annex 1					
	Category 1	Category 2	Category 3	Category 4	Category 5
LD_{50}	≤ 5 mg/kg	> 5 < 50 mg/kg	≥ 50 < 300 mg/kg	≥ 300 < 2000 mg/kg	≥ 2000 < 5000 mg/kg
Pictogram					No symbol
Signal word	Danger	Danger	Danger	Warning	Warning
Hazard statement	Fatal if swallowed	Fatal if swallowed	Toxic if swallowed	Harmful if swallowed	May be harmful if swallowed

CARCINOGENS

- ✓ Carcinogens are chemicals that have been shown to cause cancer in animals or humans.
- ✓ Chemicals labeled or noted on the MSDS as being carcinogenic, cancer-causing, potential carcinogen, or cancer suspect should be clearly labeled.

CARCINOGENS

OSHA regulated carcinogenic chemicals include:

- Chloromethyl methyl ether – vinyl chloride
- N-Nitrosodimethylamine
- N-2-Fluorenylacetamide (2-AAF)
- Benz[a]pyrene
- 4-Aminobiphenyl
- Benzidine
- 1-Naphthylamine
- 2-Naphthylamine
- 4-Nitrobiphenyl
- Benzene
- Ethylenimine
- p-Dimethylaminoazobenzene
- β-Propiolactone
- bis-Chloromethyl ether

MUTAGENS & TERATOGENS

- **Teratogen** – anything capable of disrupting normal fetal growth and producing **malformation**, e.g., drugs, poisons, radiation, physical agents such as electroconvulsive shock, infections.
- **Mutagen** – a physical or chemical agent that is capable of causing a heritable **alteration in the DNA**, which induces a **genetic mutation**, e.g., drugs, UV light, ionizing radiation.

Talidomide story

- ✓ Racemic mixture of glutamic acid 1:1 mix of enantiomers (R,S)
- ✓ R(+) acts as sedative, probably mediated by sleep receptors in the forebrain
- ✓ S(-) potently inhibits the release of alpha tumor necrosis factor (THF-α) - **teratogen**

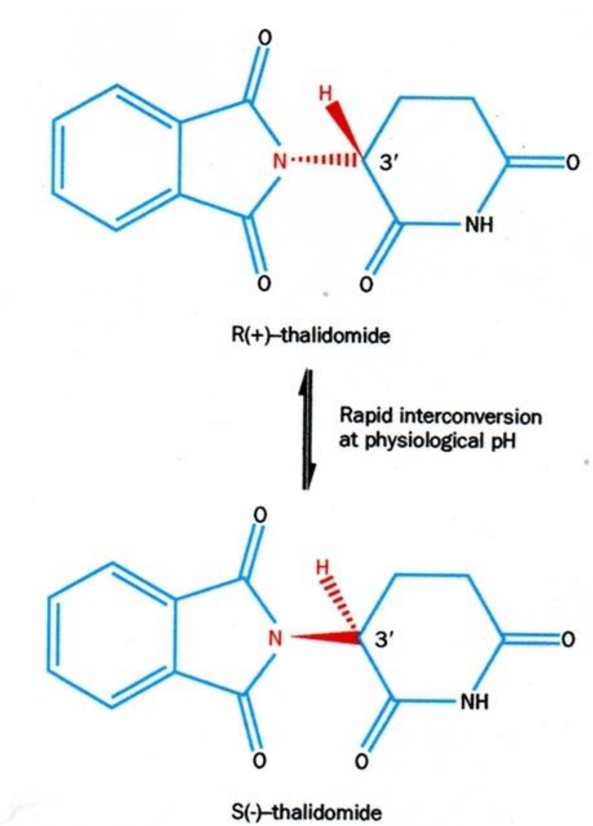


Figure 1: **Structure of thalidomide enantiomers**

The Damage

- ✓ 10,000-12,000 thalidomide babies
- ✓ 46 affected countries
- ✓ Drawn-out legal battles
- ✓ Disrupted families

REACTIVE CHEMICALS

Reactive compounds have molecular structures of high reactivity.

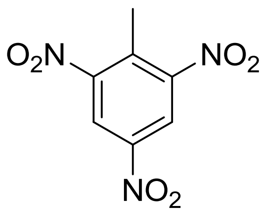
✓ **EXPLOSIVES**

- An explosive chemical is one that rapidly decomposes and produces energy that creates an explosion.
- Example: **picric acid**, in its crystalline form, is known to be explosive upon impact.
- The MSDS for each chemical received by the laboratory should be consulted for potential hazards.

✓ **OXIDIZERS**

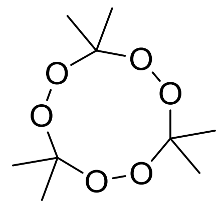
- Oxidizers are compounds which are capable of reacting with and oxidizing (i.e., giving off oxygen) other materials.
- The primary hazard associated with this class of compounds lies in their ability to act as an oxygen source, and thus to stimulate the combustion of organic materials.

Top5 EXPLOSIVES



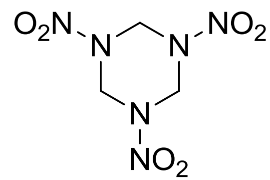
TNT

6 900 m/s



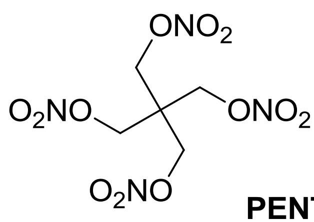
TATP

5 300 m/s



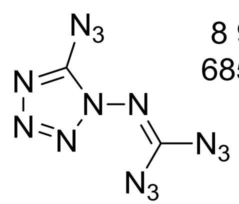
RDX

8 750 m/s
6125 kJ/kg



PENT

8 400 m/s



8 950 m/s
6855 kJ/kg

Prof. Dr. T. M. Klapotke
Angew. Chem. Int. Ed. **2011**, *50*, 4227 –4229
Chem. Asian J. **2012**, *7*, 214 – 224

Five of the most explosive non-nuclear chemicals ever made
February 17, 2017 by Laura Finney, The Conversation, Phys.Org

Preston Brown accident, January 7, 2010, Texas Tech University

Two graduate students were working on creating derivatives of an explosive compound **$Ni(N_2H_4)_5(ClO_4)_2$**. Usually, the compound is synthesized in small batches – less than 300 milligrams – but the students were concerned about variability between the batches and decided to upscale and make a single batch instead – 10 grams.

Brown lost three fingers, suffered burns to his face and hands, and damaged an eye.

Chemical & Engineering News, 2010, *88, # 34, 34-37*

COMMON OXIDIZING GROUPS	
CHEMICAL GROUP	CHEMICAL FORMULA
Peroxide	O_2^{-2}
Nitrate	NO_3^-
Nitrite	NO_2^-
Perchlorate	ClO_4^-
Chlorate	ClO_3^-
Chlorite	ClO_2^-
Hypochlorite	ClO^-
Dichromate	$Cr_2O_7^{-2}$
Permanganate	MnO_4^-
Persulfate	$S_2O_2^{-2}$

CLASSIFICATION SYSTEM FOR OXIDIZERS

CLASS RATING	HAZARD DESCRIPTION
1	An oxidizing material whose primary hazard is that it may increase the burning rate of combustible material with which it comes in contact. Examples: ▪ Potassium dichromate ▪ Silver nitrate ▪ Hydrogen peroxide (8 – 27.5%) ▪ Nitric acid (<70% conc.)
2	An oxidizing material that will moderately increase the burning rate of which may cause spontaneous ignition of combustible material with which it comes in contact. Examples: ▪ Potassium permanganate ▪ Calcium hypochlorite (<50% wt.) ▪ Hydrogen peroxide (27.5 – 52% conc.) ▪ Nitric acid (>70% conc.)

CLASSIFICATION SYSTEM FOR OXIDIZERS

CLASS RATING	HAZARD DESCRIPTION
3	An oxidizing material that will cause a severe increase in the burning rate of combustible material with which it comes contact or which will undergo vigorous self-sustained decomposition when catalyzed or exposed to heat. Examples: ▪ Potassium chlorate ▪ Hydrogen peroxide (52 – 91% conc.) ▪ Calcium hypochlorite (>50% wt.) ▪ Perchloric acid (60 – 72.5% conc.)
4	An oxidizing material that can undergo an explosive reaction when catalyzed or exposed to heat, shock, or friction. Examples: ▪ Ammonium perchlorate ▪ Guanidine nitrate ▪ Hydrogen peroxide (>91% conc.) ▪ Perchloric acid (>72.5%)

REMEMBER these things about oxidizers:

- The primary hazard is the ability to act as an oxygen source, especially hazardous during fire situation.
- These materials present a fire and explosion hazard when in contact with organic or combustible materials. All contact with organic or combustible material must be avoided.
- They are generally corrosive.
- The hazards associated with the use of perchloric acid are particularly severe.

REMEMBER these things about oxidizers:

- ✓ Perchloric acid may NOT be used in any hood except those specially designed for perchloric acid use.
- ✓ Strong oxidizing agents, such as chromic acid, should be stored and used in glass or other inert, and preferably unbreakable, containers.
- ✓ Corks or rubber stoppers must NEVER be used.
- ✓ Reaction vessels containing appreciable amounts of oxidizing materials should never be heated in oil baths, but rather on a heating mantle or sand baths.

Other reactive chemicals

- ✓ Compounds with redox groups (hydrazine, hydroxylamine)
- ✓ Compounds that react violently with water or air (anhydrous metal oxides)
- ✓ Pyrophoric compounds that spontaneously react with air
- ✓ Compounds that form peroxides over time and become explosive – such as diethyl ether.

CHEMICAL STORAGE

- **Avoid storing materials and equipment on top of cabinets**
- Do not store corrosive liquids above eye level.
- Provide a specific storage location for each type of chemical, and return the chemicals to those locations after each use.
- Avoid storing chemicals in the workspace within a laboratory hood, except for those chemicals currently in use.
- If a chemical does not require a ventilated cabinet, store it inside a closable cabinet or on a shelf that has a lip to prevent containers from sliding off in the event of an accident or fire.
- Do not expose chemicals to heat or direct sunlight.
- Observe all precautions regarding the storage of incompatible chemicals.
- **Use corrosion resistant storage trays or secondary containers to collect materials if the primary container breaks or leaks.**
- **Do not store flammable liquids in a refrigerator unless it is approved for such storage. Such refrigerators are designed with non-sparking components to avoid an explosion.**

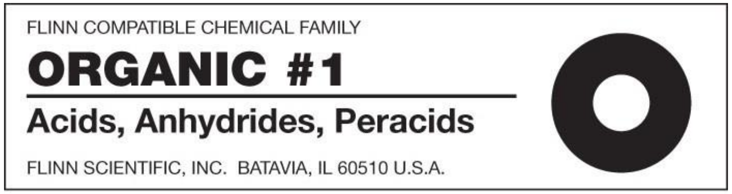
Ohio State University accident, April 8, 2005

A Solvent cabinet shelf collapses, spilling a large volume of hexane (> 12L) which eventually ignites. The explosion could have been triggered by any number of ignition sources, including static electricity or a spark from a motor or switch.

The lab was, in fact, completely destroyed, including all of the research, lab notes, and other work by Coleman and his students. The Coleman group studies antitumor agents, including the bacterial agents azinomycins A and B.

Chemical & Engineering News, *2005, 83, #21, pp. 34-35*

CHEMICAL STORAGE

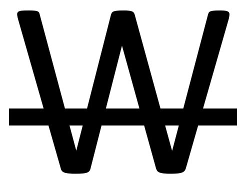


I1 – Metals, Hydrides
I2 – Acetates, Halides, Iodides, Sulfates, Sulfites, Thiosulfates, Phosphates, Halogens
I3 – Amides, Nitrates (except Ammonium Nitrate), Nitrites, Azides
I4 – Hydroxides, Oxides, Silicates, Carbonates, Carbon
I5 – Sulfides, Selenides, Phosphides, Carbides, Nitrides
I6 – Chlorates, Bromates, Iodates, Chlorites, Hypochlorites, Perchlorates, Perchloric Acid, Peroxides, Hydrogen Peroxide
I7 – Arsenates, Cyanides, Cyanates
I8 – Borates, Chromates, Manganates, Permanganates
I9 – Acids (except Nitric) Nitric Acid is isolated and stored by itself.)
I10 – Sulfur, Phosphorus, Arsenic, Phosphorous Pentoxide
IM – Miscellaneous

O1 – Acids, Amino Acids, Anhydrides, Peracids
O2 – Alcohols, Glycols, Sugars, Amines, Amides, Imines, Imides
O3 – Hydrocarbons, Esters, Aldehydes, Oils
O4 – Ethers, Ketones, Ketenes, Halogenated Hydrocarbons, Ethylene Oxide
O5 – Epoxy Compounds, Isocyanates
O6 – Peroxides, Hydroperoxides, Azides
O7 – Sulfides, Polysulfides, Sulfoxides, Nitriles
O8 – Phenols, Cresols
O9 – Dyes, Stains, Indicators
OM – Miscellaneous

CHEMICAL STORAGE

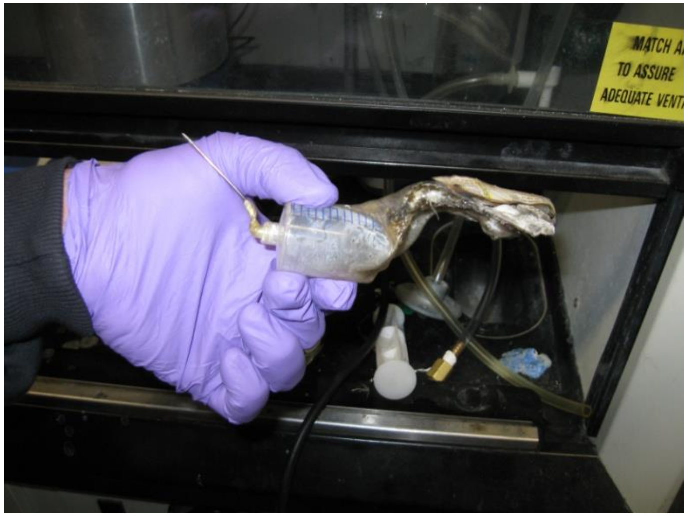
- ✓ Water-reactive chemicals such as sodium, potassium, and metal hydrides should be segregated from other chemicals and stored in a dry environment.
- ✓ These areas should NOT be equipped with sprinkler systems.



Sheharbano Sangji lab accident (USLA, 12/29/2008)

t-Butyl lithium, ignites on contact with air. Sangji was working was not wearing protective clothing. Died from third-degree burns over 40 percent of her body after her sweater caught fire as she tried to transfer a notoriously flammable liquid from one container to another.

Her supervisor, Prof. Patric Harran, charged with four felony counts of willfully violating state occupational health and safety standards, had faced up to 4-1/2 years in prison if convicted.



Los Angeles Times, December 16, 2015

TRANSPORTING CHEMICALS

- Use a bottle carrier, cart or other **secondary container** when transporting chemicals in breakable containers (especially 250 ml or more) through hallways or between buildings. Secondary containers are made of rubber, metal or plastic, with carrying handle(s), and are large enough to hold the entire contents of the chemical containers in the event of breakage.
- Transport of hazardous chemicals in individual containers exceeding four liters between buildings is strongly discouraged.
- When moving in the laboratory, anticipate sudden backing up or changes in direction by others. If you should stumble or fall while carrying glassware or chemicals, try to project them away from yourself and others.
- The individual transporting the chemical should be knowledgeable about the hazards of the chemical and should know how to handle a spill of the material. (SDS)
- **When transporting compressed gas cylinders, the cylinder should always be strapped in a cylinder cart and the valve protected with a cover cap. Do not attempt to carry or roll cylinders from one area to another.**
- Keep chemicals in their original packing when transporting, if possible.

REACTION HAZARD

Scale-up and potential runaway reactions

During a research career, the need to synthesize larger quantities of a specific chemical is likely. This scale-up may alter reaction kinetics unpredictably and may create conditions under which a reaction vessel can self-heat more than passive cooling can dissipate away, creating a thermal runaway reaction.

Catalyst effects on reactions

Whenever a catalyst is added to a reaction, the reaction rate changes, as does the rate of generation of heat and byproducts. Separating some catalysts from reaction mixtures may cause fires.

REACTION HAZARD

Reactive and unstable chemicals	Students should be able to explain what makes chemicals reactive or unstable, including both explosive chemicals and reactions that could lead to explosions. Pyrophoric chemicals require special techniques for handling, and students must be trained specifically in these techniques if they are to use these chemicals. Chemicals that react with air or water, such as phosphorus oxychloride (POCl3), sodium metal (Na), or acetic anhydride (Ac2O), require special handling to address their reactive hazards. Also included are chemicals that become unstable over time, such as cyclic polyenes or some alkyne structures.
Peroxides and peroxideforming chemicals	Students should be able to explain peroxide reactivity and the types of chemicals that form peroxides spontaneously at varying rates. Most –C–O–C– compounds that contain an activated α-hydrogen will slowly react to form the corresponding peroxide –C–O–O–C–, which may be violently unstable.

Walter Partlo lab accident, June 17, University of Minnesota

He was making trimethylsilyl azide, starting with 200 g of sodium azide. There are no engineering controls available in the department that would allow the reaction to be performed safely at 200 g scale. The limit was 5 g.

The student injured his arm and side, and he needed surgery to deal with glass shards. The student also injured an eardrum. He was not severely burned.

Org. Synth. **1970**, *50*, 107

$$Me_3SiCl \xrightarrow[\text{diglyme}]{NaN_3} Me_3SiN_3$$

Caution! This reaction should be conducted behind a safety shield in a fume hood. In the presence of water and certain other proton sources, highly toxic hydrazoic acid may form which also poses an explosion hazard. [Note revised, August 2014].

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

FIRE SAFETY

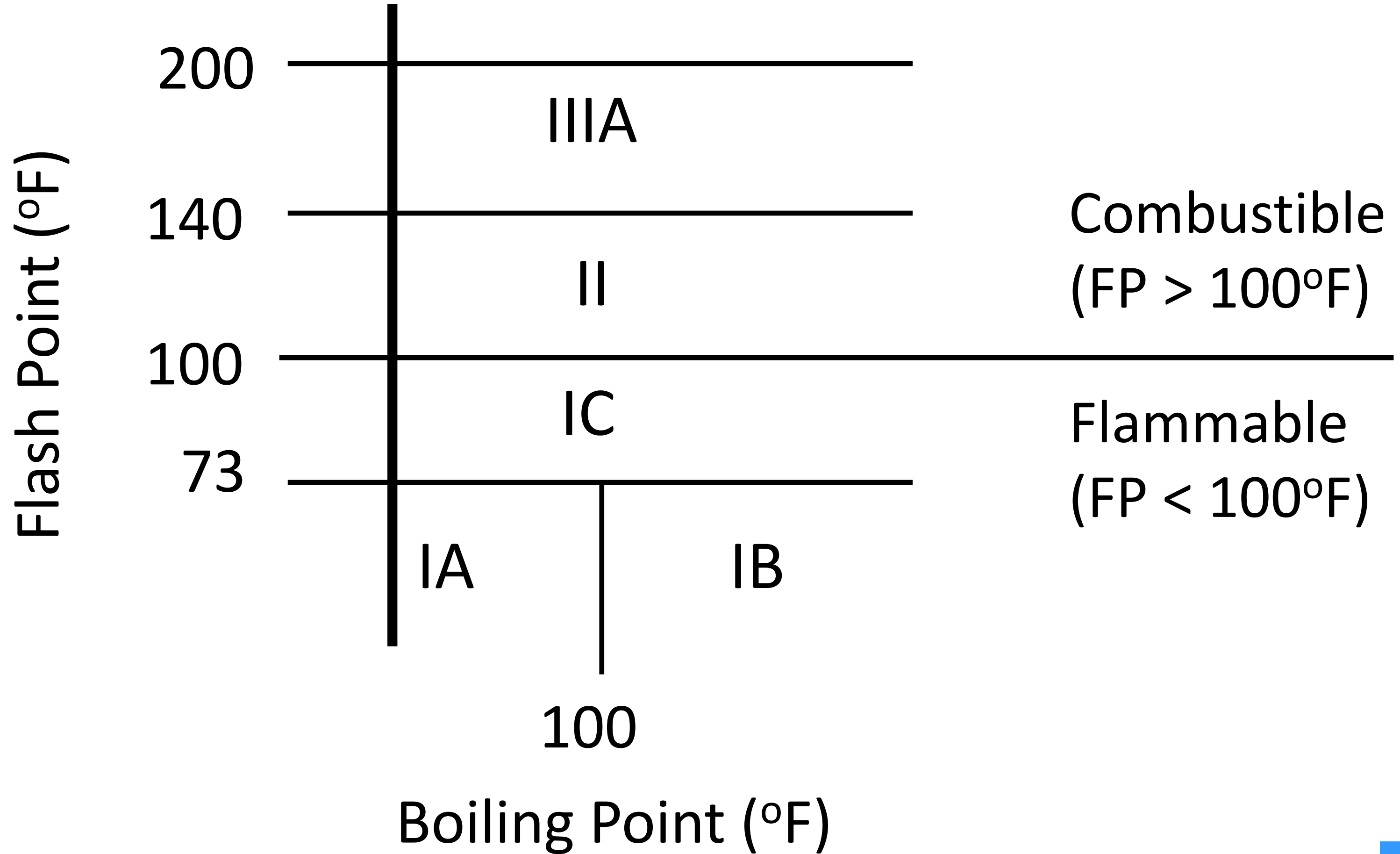
FLAMMABLE & COMBUSTIBLE CHEMICALS

- ✓ Flammable and combustible liquids, which are used in numerous routine procedures, are among the most hazardous materials in the clinical chemistry laboratory because of possible fire or explosion.
- ✓ They are classified according to **flashpoint**

FIRE SAFETY

- **Flash point** means the minimum temperature at which a liquid gives off vapor within a test vessel in sufficient concentration to form an ignitable mixture with air near the surface of the liquid.
- In general, the lower the flash point, the greater the hazard
- **Flammable liquids** have flash points at or below 199.4^{o}F (93^{o}C)

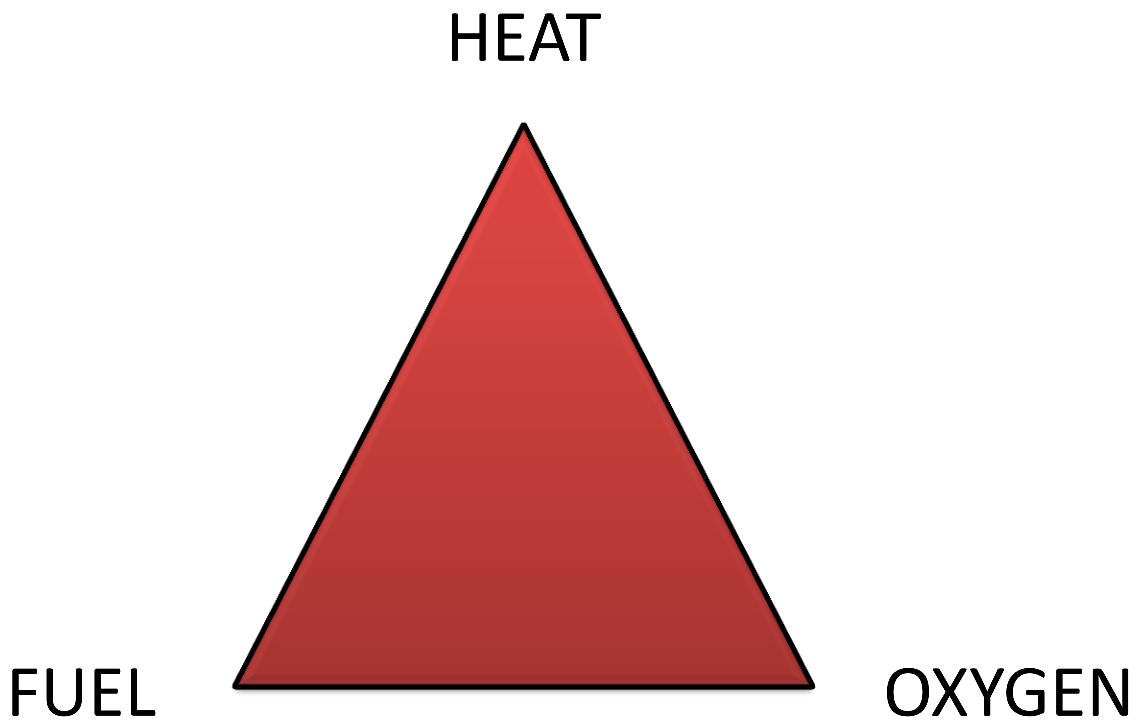
Categories of Flammable Liquids



FIRE SAFETY

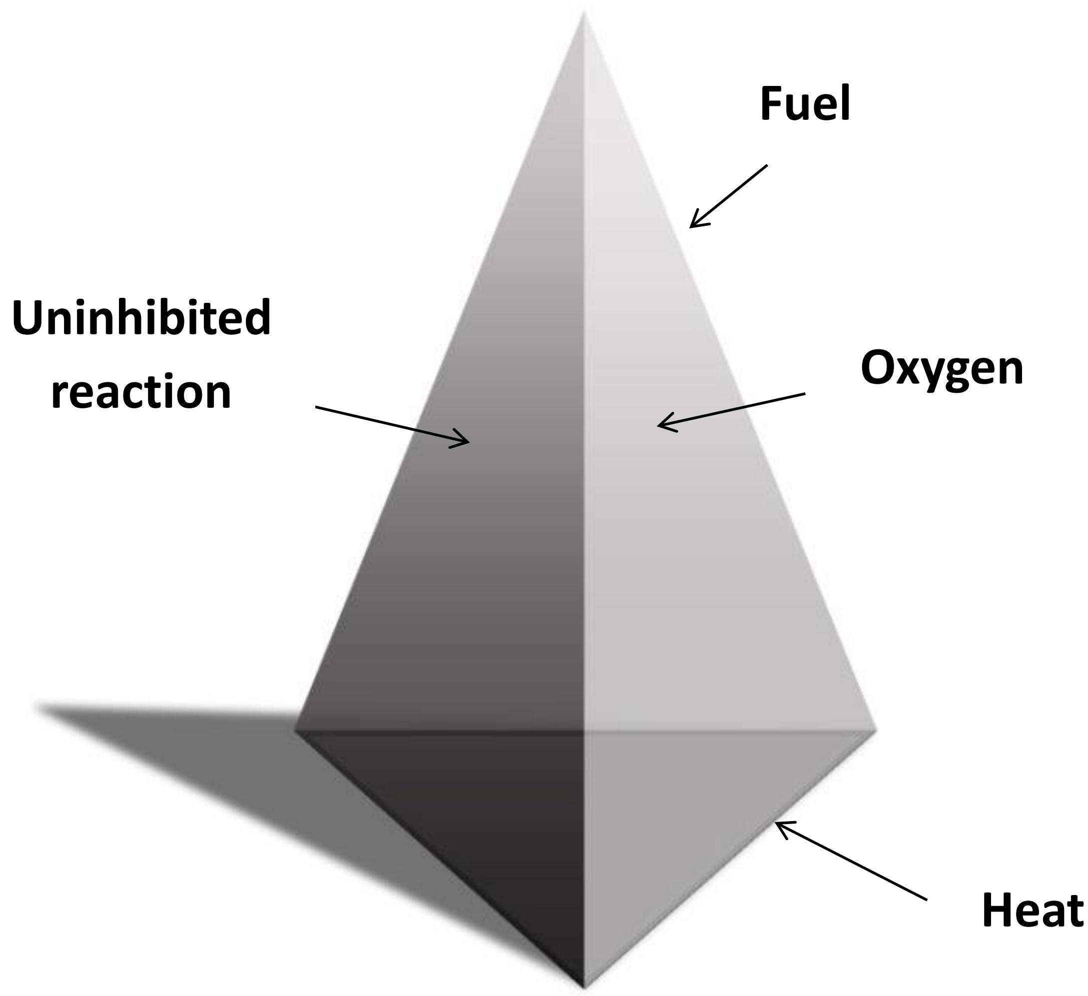
	Common Name	Flash Point
CLASS IA	Ethyl Ether	-49
CLASS IB	Gasoline	-45
	Methyl Ethyl Ketone	21
	Toluene	40
CLASS IC	Xylene	81-115
	Turpentine	95

FIRE SAFETY



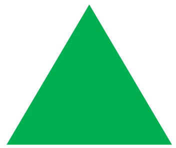
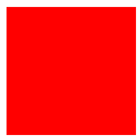
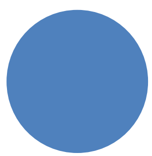
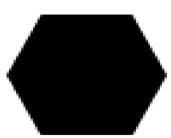
FIRE TRIANGLE

FIRE SAFETY

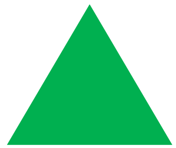
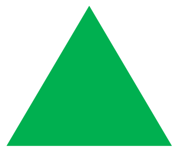
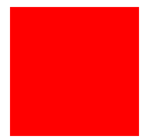
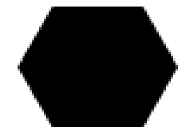
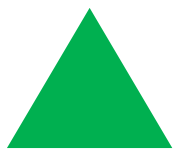
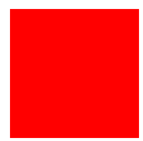
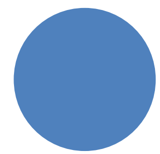
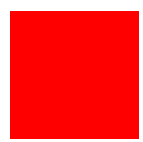
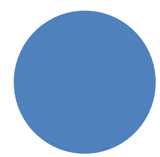
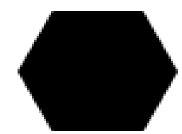


The Fire Tetrahedron

FIRE SAFETY

FIRE CLASS	GEOMETRIC SYMBOL	PICTOGRAM / PICTURE SYMBOL		INTEDED USE
A		Garbage can and wood pile burning		Ordinary solid combustibles
B		Fuel container and burning puddle		Flammable liquids and gases
C		Electric plug and burning outlet		Energized electrical equipment
D				Combustible metals
K		Pan burning		Cooking oils and fats

FIRE SAFETY

TYPE	SUITABLE FOR USE ON FIRE CLASSES				
WATER					
FOAM					
DRY CHEMICAL (POWDER)					
CARBON DIOXIDE					
CLASS D POWDER					

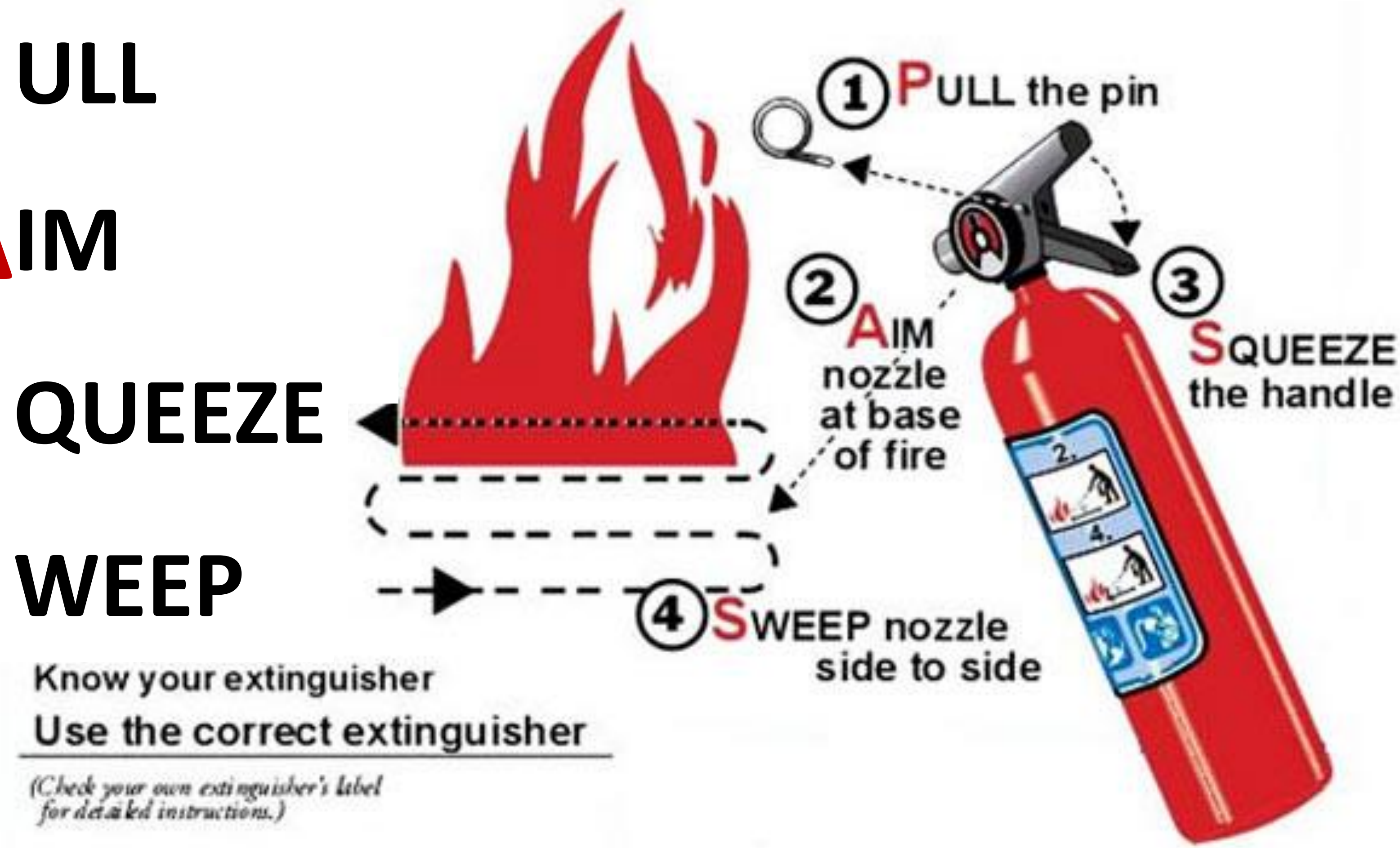
To operate a fire extinguisher:

P ULL

A IM

S QUEEZE

S WEEP



Meng Xiangjian accident, 18 December 2015, Tsinghua University

The researcher, Meng Xiangjian, died after a hydrogen storage cylinder unexpectedly exploded at Ho Tim building, in the centre of the university's Beijing campus

Nature, doi:10.1038/nature.2015.19066

ELECTRICAL SAFETY

ELECTRICAL SAFETY

- ✓ Laboratories have a great deal of electrical equipment in proximity to sinks, liquids or other grounded surfaces.
- ✓ **HAZARDS**:
    1. **Burns**
    2. **Shock**
    3. **Electrocution**
    4. **Ignition**
    5. **Explosion**
- ✓ Fire and explosion hazards are avoided by preventing the occurrence of high temperatures.
- ✓ **Circuit breakers, fuses, and ground fault interrupters (GFI)** are designed to detect overloaded circuits that could cause ignition and explosion.

Precautionary Measures

- ✓ Use only explosion-proof equipment in hazardous atmospheres.
- ✓ Be particularly careful when operating high-voltage equipment, such as electrophoresis apparatus.
- ✓ Use only properly grounded equipment (three-prong plug).
- ✓ Check for frayed electrical cords.
- ✓ Promptly report any malfunctions or equipment producing a “tingle” for repair.

Precautionary Measures

- ✓ Do not work on “live” electrical equipment.
- ✓ Never operate electrical equipment with wet hands.
- ✓ Know the exact location of electrical control panel for the electricity to your work area.
- ✓ The use of extension cords is NOT ALLOWED. In emergency situations, use only approved extension cords (properly grounded, heavy-duty) and do not overload circuits.
- ✓ Have ground checks and periodic preventive maintenance performed on equipment.

COMPRESSED GASES

COMPRESSED GASES

- ✓ Compressed gas cylinders of varying sizes can be found in laboratories and especially in research laboratories.
- ✓ Since the **cylinders are pressurized**, they can become "torpedoes" that can even penetrate block walls if the main valve stem is sheared by falling over.
- ✓ A good working practice when using a flammable gas is to allow only one cylinder of gas to be in use at a time and to **use the smallest size possible.**

COMPRESSED GASES

- ✓ Gas cylinders, both flammable and non-flammable, should never be stored in fire safety cabinets with flammable and combustible liquids.
- ✓ They should be grouped by type and stored in a ventilated room reserved exclusively for cylinder storage. The room should have a fire resistance rating of at least 2 hours.

COMPRESSED GASES

- ✓ Cylinders should always be secured by a chain or other device to prevent them from falling over and shearing the valve stem.
- ✓ When cylinders are transported, valve protective caps should be used.
- ✓ When cylinders are not in use, the valves should be tightly closed.

COMPRESSED GASES

Precautionary Measures

- ✓ Know the gas that you will use.
- ✓ Store tanks in a vertical position.
- ✓ Keep cylinders secured at all times.
- ✓ Never store flammable liquids and compressed gases in the same area.
- ✓ Use the proper regulator for the type of gas in use.
- ✓ Do not attempt to control or shut off gas flow with the pressure relief regulator.
- ✓ Keep removable protection caps in place until the cylinder is in use.

Precautionary Measures

- ✓ Make certain that acetylene tanks are properly piped (the gas is incompatible with copper tubing).
- ✓ Do not force a “frozen” or stuck cylinder valve.
- ✓ Use a hand truck to transport large tanks.
- ✓ Always check tanks on receipt and then periodically for any problems such as leaks.

Precautionary Measures

- ✓ Make certain that the cylinder is properly labeled to identify the contents.
- ✓ Empty tanks should be marked “EMPTY”.

Thea Ekins-Coward accident, March 16, University of Hawaii

Postdoctoral researcher Thea Ekins-Coward, 29, **lost an arm and suffered other injuries** in a lab explosion at the University of Hawaii (UH), Mānoa on March 16.
At the time of the incident, she was combining H2, CO2, and O2 from high-pressure cylinders into a lower pressure container. The mixture was to be used to feed bacteria. Since 2008, when the project began, the process has been used almost daily and without incident.

Chemical & Engineering News, 2016, 94, #13, p. 6

CRYOGENIC MATERIALS

CRYOGENIC MATERIALS

- ✓ **Liquid nitrogen** – probably one of the most widely used cryogenic fluids (liquefied gases) in the laboratory.
- ✓ **Hazards** of cryogenic material:
  - Fire or explosion
  - Asphyxiation
  - Pressure build-up
  - Embrittlement of materials
  - Tissue damage (similar to that of thermal burns)

Precautionary Measures

- ✓ Only containers constructed of materials designed to **withstand ultralow temperatures** should be used for cryogenic work.
- ✓ The use of **eye/face protection**, hand protection to guard against the hazards of touching super-cooled surfaces is recommended.
- ✓ The **gloves, of impermeable material**, should **fit loosely** so that they can be taken off quickly if liquid spills on or into them.

Precautionary Measures

- ✓ To minimize violent boiling/frothing and splashing, specimens to be frozen should always be inserted into the coolant very slowly.
- ✓ Cryogenic fluids should be stored in well-insulated but loosely stoppered containers that minimize loss of fluid resulting from evaporation by boil-off and that prevent plugging and pressure build-up.

MECHANICAL AND ERGONOMIC HAZARDS

MECHANICAL HAZARDS

- ✓ **Centrifuges** – must be balanced to distribute the load equally
- ✓ **Autoclaves** – steam under pressure
- ✓ **Homogenizers**
- ✓ **Laboratory glassware** – be careful in handling breakable and sharp objects
- ✓ **Sharp instruments** – dispose in puncture-resistant containers

Repetitive strain disorders:

1. Tenosynovitis
2. Bursitis
3. Ganglion cysts
4. Acute musculoskeletal injury

✓ **Primary contributing factors** associated with repetitive strain disorders:

- Position / posture
- Applied force
- Frequency of repetition

Michele Dufault accident, 13 April, 2011, Yale University

In the early hours of 13 April, undergraduate students working at Yale University's Sterling Chemistry Laboratory made a shocking discovery. There in the lab's machine shop was the dead body of 22-year-old undergraduate student Michele Dufault, her hair tangled in a lathe. She had died of asphyxiation.

Nature 472, 270-271 (2011) | doi:10.1038/472270a

DISPOSAL OF HAZARDOUS MATERIALS

CHEMICAL WASTES

- ✓ In some cases, it is permissible to flush water-soluble substances down the drain with copious quantities of water.
- ✓ Strong acids and bases should be neutralized before disposal.
- ✓ Foul-smelling chemicals should never be flushed down the drain.
- ✓ Other liquid wastes, including flammable solvents, must be collected in approved containers and segregated into compatible classes.

CHEMICAL WASTES

- ✓ Flammable material can also be burned in specially designed incinerators with afterburners and scrubbers to remove toxic products of combustion.
- ✓ Before disposal, hazardous substances that are explosive, such as carcinogens and peroxides, should be transformed into less hazardous forms whenever feasible.
- ✓ Solid chemical wastes that are unsuitable for incineration must be buried in a landfill. This practice, however, has created an environmental problem, and there is now a shortage of safe sites.

University of Maryland accident, September 26, 2011

Students were conducting an experiment using nitric acid and sulfuric acid. The combination of these 2 acids does not normally cause such a violent reaction, however, when the combined product was introduced into a chemical waste container; a violent chemical reaction occurred causing an explosion with fire.

The two students and the 2 UMD employees were de-contaminated on the scene and treated by paramedics on the scene. The students were soon transported to an area Burn Unit for treatment. They were transported in good condition. The UMD employees did not require hospitalization.

The Washington Times - Monday, September 26, 2011

ACCIDENT ACTION

CONCENTRATED ACID / BASE SPILLS

- ✓ Dilute first with water before clean-up is attempted.
- ✓ The spill should then be covered with a neutralizer:

  Boric acid – for bases

  Sodium bicarbonate – for acids
- ✓ The spill should then be absorbed with an absorbent material.

CONCENTRATED ACID / BASE SPILLS

- ✓ Dispose according to the institutional policy on chemical waste disposal.
- ✓ The surface should then be cleansed with soap and water after the chemical is cleaned up.

SOLVENT SPILLS

- ✓ If a solvent is spilled, no water or diluent should be added and the solvent should not be allowed to flow down a drain.
- ✓ Since solvents may present a fume problem, respiratory protective equipment needs to be available.
- ✓ After absorption with absorbent material, the material should be placed in a closed container to prevent fumes from escaping.
- ✓ All containers should be labeled with the chemical name and any hazard and disposed as chemical waste.

CHEMICALS SPILLS

Category	Size	Response	Treatment Materials
Small	up to 300cc	chemical treatment or absorption	neutralization or absorption spill kit
Medium	300 cc - 5 liters	absorption	absorption spill kit
Large	more than 5 liters	call public safety	outside help

Spill Cleanup Procedures

Absorbent Pad Spill Kit

1 Place a barrier around the spill and **use tongs** to remove any broken glass

2 Cover the spill completely with appropriate material

3 Wait a few minutes for spill to absorb and then clean

4 Bag and tag for EH&S waste removal

Floor Dry Spill Kit

Chemicals on Skin or Clothing

- Immediately flush with water for no less than 15 minutes.
- For larger spills, the safety shower should be used.
- While rinsing, quickly remove all contaminated clothing or jewelry. **Seconds count. Do not waste time because of modesty.**
- Use caution when removing pullover shirts or sweaters to prevent contamination of the eyes.
- Check the Safety Data Sheet to determine if any delayed effects should be expected.
- Discard contaminated clothing or launder them separately from other clothing. Leather garments or accessories cannot be decontaminated and should be discarded.
- **Do not use solvents to wash skin**. They remove the natural protective oils from the skin and can cause irritation and inflammation. In some cases, washing with a solvent may facilitate absorption of a toxic chemical.
- For flammable solids on skin, first brush off as much of the solid as possible, then proceed as described above.
- Fill out an Incident Report!

Chemicals in Eyes

- Immediately flush eye(s) with water for at least fifteen minutes. The eyes must be forcibly held open to wash, and the eyeballs must be rotated so all surface area is rinsed. The use of an eye wash fountain is desirable so hands are free to hold the eyes open. If an eyewash is not available, pour water on the eye, rinsing from the nose outward to avoid contamination of the unaffected eye.
- Remove contact lenses while rinsing. **Do not lose time removing contact lenses before rinsing.** Do not attempt to rinse and reinsert contact lenses.
- Seek medical attention regardless of the severity or apparent lack of severity. Explain carefully what chemicals were involved. If easily accessible, bring an SDS.

When Chemical Exposure Occurs Seconds Count!

Thank you for attention