Laboratory Safety – Tips and Case Studies

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Objectives

• Chemical inventory
• High hazard chemicals
• Chemical storage
• Chemical labeling - Globally Harmonized System
• Hazardous waste
• No fly zones
• Self inspections
CHEMICAL INVENTORY
Chemical Inventory

• A critical first step. Don’t skip it
• Handwritten or inventories in Word are not as useful as Excel, which allows for the filters, sorting, and aggregation.
• Recommended minimum:
  – Chemical name
  – CAS number
  – Manufacturer/product number (if a product as opposed to pure chemical)
  – Location
  – Hazard class(es)
  – Amount of material (assume full container)
## Spreadsheets / One Hazard Column

<table>
<thead>
<tr>
<th>Label name</th>
<th>CAS</th>
<th>State</th>
<th>Room</th>
<th>No</th>
<th>Size</th>
<th>Manufacturer</th>
<th>Product</th>
<th>Hazard</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abscisic acid</td>
<td>14375-45-2</td>
<td>solid</td>
<td>309</td>
<td>1</td>
<td>100 mg</td>
<td>Sigma</td>
<td>7773-56-0</td>
<td>IRR</td>
</tr>
<tr>
<td>Abscisic acid</td>
<td>14375-45-2</td>
<td>solid</td>
<td>309</td>
<td>1</td>
<td>100 mg</td>
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<td>100 mg</td>
<td>Sigma</td>
<td>7773-56-0</td>
<td>IRR</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>75-07-0</td>
<td>liquid</td>
<td>333</td>
<td>1</td>
<td>100 g</td>
<td>M/CB</td>
<td>AX25</td>
<td>FL</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>75-07-0</td>
<td>liquid</td>
<td>333</td>
<td>1</td>
<td>100 g</td>
<td>M/CB</td>
<td>AX25</td>
<td>FL</td>
</tr>
<tr>
<td>Acetamide</td>
<td>60-30-5</td>
<td>crystal</td>
<td>333</td>
<td>1</td>
<td>1 lb</td>
<td>Mallinc</td>
<td></td>
<td>IRR</td>
</tr>
<tr>
<td>Acetamide</td>
<td>60-30-5</td>
<td>crystal</td>
<td>333</td>
<td>1</td>
<td>1 lb</td>
<td>Mallinc</td>
<td></td>
<td>IRR</td>
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<tr>
<td>Benzene</td>
<td>71-43-2</td>
<td>liquid</td>
<td>320</td>
<td>1</td>
<td>10 ml</td>
<td>Sigma</td>
<td></td>
<td>FL, TOX</td>
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</tbody>
</table>
## Spreadsheets / Multiple Hazard Columns

<table>
<thead>
<tr>
<th>Label name</th>
<th>CAS</th>
<th>State</th>
<th>…………</th>
<th>Fire Code 1</th>
<th>Fire Code 2</th>
<th>DOT hazard</th>
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</thead>
<tbody>
<tr>
<td>Abscisic acid</td>
<td>14375-45-2</td>
<td>Solid</td>
<td>…………</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Abscisic acid</td>
<td>14375-45-2</td>
<td>solid</td>
<td>…………</td>
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<td>-</td>
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<tr>
<td>Abscisic acid</td>
<td>14375-45-2</td>
<td>solid</td>
<td>…………</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>75-07-0</td>
<td>liquid</td>
<td>…………</td>
<td>FL-1A</td>
<td>Carcin</td>
<td>3</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>75-07-0</td>
<td>liquid</td>
<td>…………</td>
<td>FL-1A</td>
<td>Carcin</td>
<td>3</td>
</tr>
<tr>
<td>Acetamide</td>
<td>60-30-5</td>
<td>crystal</td>
<td>…………</td>
<td>Irritant</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetamide</td>
<td>60-30-5</td>
<td>crystal</td>
<td>…………</td>
<td>Irritant</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>71-43-2</td>
<td>Liquid</td>
<td>…………</td>
<td>FL-1B</td>
<td>Carcin</td>
<td>3</td>
</tr>
</tbody>
</table>
Database for Large Inventories

Substance info.
Manufacturer/product info.
Location and amount of material

Screen shot: Item Record
### Database for Large Inventories

**Cal/OSHA carcinogen**
- Prop 65

**Hazards**
- Fire Code hazards
- DOT hazards
- GHS Hazards

**Substance: 75-09-2 / METHYLENE CHLORIDE**

<table>
<thead>
<tr>
<th>Category</th>
<th>Classification</th>
<th>Classification text</th>
</tr>
</thead>
<tbody>
<tr>
<td>CA fire hazard 01</td>
<td>Carcinogen*</td>
<td></td>
</tr>
<tr>
<td>DOT hazard 01</td>
<td>6.1 Poisonous materials</td>
<td>Harmful; Xn</td>
</tr>
<tr>
<td>EC classification 01</td>
<td>R40</td>
<td></td>
</tr>
<tr>
<td>EC risk 01</td>
<td>S2</td>
<td>Limited evidence of a carcinogen</td>
</tr>
<tr>
<td>EC safety 01</td>
<td></td>
<td>Keep out of the reach of children</td>
</tr>
</tbody>
</table>

**Screen shot: Substance**
HIGH HAZARD CHEMICALS
## Physical and Health Hazards

### Physical Hazards

- A chemical is a physical hazard if it is:
  - Flammable
  - Combustible
  - Explosive
  - Oxidizing
  - Pyrophoric
  - Reactive (including water reactive)
  - Organic peroxide
  - Compressed gas

### Health Hazards

- Acute hazards produce prompt or only slightly delayed effects such as serious burns, respiratory system inflammation, or eye irritation
- Chronic hazards produce effects only from repeated exposure over time which may involve cumulative damage to different organs or parts of the body (e.g., noise)
Flammable Liquids

• Ethanol and isopropanol are some examples
• Involved in many lab fires and explosions
• Separate from ignition sources
• Store flammables in approved flammable cabinets – with latch door
• Keep a minimum amount outside of flammable cabinets
• Monitor to avoid exceeding fire code limits
Texas Tech University: 1 gallon of solvent in a hood

Notice open bottles in other hood
Compressed Gases

• Toxic gases (e.g., carbon monoxide, hydrogen sulfide)
  – Poisonings
  – Building evacuations
  – Toxic air contaminants (TAC)
    • Nitric acid in an open bath is a no no!

• Flammable gases (e.g., acetylene, hydrog
  – Cause many lab fires and explosions
  – May require monitoring
Compressed Gas Incidents

Toxic gases are often used in organic synthesis.

Hydrogen fluoride lecture bottle that exploded.
Compressed Gas Safety

- Aside from the hazard of the gas, these items also present a physical and asphyxiation hazard.
- Store and handle in well ventilated area.
- Keep cylinders secured at all times. Secure at top and bottom 1/3 of cylinder.
- Never connect or disconnect regulators without receiving training.
- Label tubes with name and direction of flow.
- Use a cylinder cart when transporting cylinders.
Cryogenic Liquid Safety

- Liquid nitrogen and liquefied carbon dioxide are examples.
- Can destroy living tissue.
- Store and handle in well ventilated area.
- Never connect or disconnect containers of cryogenic material without receiving training.
- Keep dewars secured at all times. Use chains at top and bottom of dewar.
- Wear appropriate PPE whenever handling this material:
  - Face shield and safety glasses with side shields or goggles.
  - Insulated and non-absorbent gloves which are loose fitting.
  - High top shoes /no openings and constructed of non-porous material.
  - Rubber apron.
- Only use containers approved for cryogenic material.
Reactive Chemicals

**Water–reactives**
- Upon mixing with water, can produce:
  - Flammable gas (lithium, sodium, potassium)
  - Toxic gas (phosphide, phosphorus pentachloride)
  - Violent reactions (sodium hydroxide)
- Accidents during chemical synthesis and storage

**Pyrophorics (air reactives)**
- Many are also water reactive
- Common pyrophorics include: phosphine, phosphorus, palladium, zinc dust, sodium methoxide
- Accidents during chemical synthesis and storage
Safety Training

Explosive (by contamination or improper storage)

- Produced as by-products by reacting with metals or initiated by heat
  - Heavy metal azides
    - Could be formed by pouring sodium azide into sink!
  - Perchlorates with heavy metals
  - 1-Hydroxybenzotriazole (heat)
  - Nitromethane (heat)

- Result from aging or improper storage of chemicals
  - Picric acid if dry
  - Peroxide formers (e.g. tetrahydrofuran, ethyl ether)

Explosive byproducts can be formed. Train to “plan for safety”
Peroxide – Former Explosion

Source: University of California, Berkeley, Office of Environment Health and Safety, Lessons Learned
<table>
<thead>
<tr>
<th>&lt; 25 ppm</th>
<th>Considered safe for general use</th>
</tr>
</thead>
<tbody>
<tr>
<td>25-100 ppm</td>
<td>Not recommended for distilling or otherwise concentrating</td>
</tr>
<tr>
<td>&gt;100 ppm</td>
<td>Avoid handling and contact your safety person for assistance with safe disposal</td>
</tr>
</tbody>
</table>

Tetrahydrofuran
Ethyl ether

- If unopened from manufacturer, up to 18 months or stamped expiration date, whichever comes first.
- After opening, materials should be discarded or evaluated for peroxides within 12 months.
A Tragic Accident - Pyrophorics

- A young researcher died as a result of severe burning caused by transferring t\textsuperscript{-}butyl lithium (pyrophoric)

- Lessons Learned:
  - Provide adequate training and supervision
  - Have and enforce a “No Working Alone” Policy
  - Wear proper PPE
“Dirty Dozen” Chemicals

- Organic azides
- Perchlorate salts of organic, organometallic, and inorganic complexes
- Diethyl ethers
- Lithium aluminum hydride
- Sodium, potassium
- Potassium metal
- Sodium-benzophenone ketyl still pots
- Palladium on carbon
- Heat generated from exothermic reactions
- Ethers with alpha hydrogen atoms
- Carbon monoxide
- Organic peroxides

Particularly Hazardous Substances

- **Acutely toxic compounds**
  - LD50 < 200 mg / kg
  - Arsenic compounds (phenylarsine oxide, sodium arsenite),
  - Mercury, lead, cadmium salts
  - Cyanides (potassium cyanide)

- **Carcinogens**
  - Carcinogen Report of Use
    - ≥ 0.1% by weight or volume (1,000 ppm)
    - Methylene chloride
    - Formaldehyde
    - Chromium
    - Cadmium
    - Benzene

- **Reproductive and developmental toxins**
  - Arsenic, beryllium, benzene, lead, toluene, N,N-Dimethylformamide (DMF)
Particularly Hazardous Substances

- Maintain the lowest possible quantities of these.
- Try to order as a solution rather than powder/solid.
- Designate area to use these.
- Containers should be tightly sealed.
- Handle in a fume hoods if possibility of inhalation exposure.
- Promptly cleanup any spill and dispose as hazardous waste.
A Tragic Death – Organomercury poisoning

- Dartmouth Professor Karen Wetterhahn
- Death from organomercury poisoning (dimethylmercury)
- Lessons Learned:
  - Wear proper PPE (e.g., silver shield gloves not latex)
  - Make sure the PPE is acceptable for the chemical and its use
Brain Teaser

- Which of the following may require a Cal/OSHA carcinogen use notification:
  - Chromic oxide
  - Benzene
  - Arsenic trioxide
  - Methylene chloride
Brain Teaser

- ALL OF THESE may need to be reported!
  - Chromic oxide
  - Benzene
  - Arsenic trioxide
  - Methylene chloride
CHEMICAL STORAGE TIPS
Chemical Safety Tips

• Keep containers closed.
• Promptly put away all hazardous chemicals that are not in use.
  – Make sure cabinets are labeled too.
• Provide adequate secondary containment.
  – Required of corrosives, flammables, and reactives.
  – Required of all hazardous waste liquids.
• Do not store chemicals near the sink.
Chemical Safety Tips

• Do not store incompatible chemicals together.
• Regularly inspect storage areas.
• Use a carrying container or cart with a lip for moving chemicals around.
California is Earthquake County
Chemical Safety Tips

- Seismic security of chemical storage cabinets
- Lips on chemical shelves
Brain Teaser

- What chemical would you expect to find here?
  - Sodium perchlorate
  - Sodium hydroxide
  - Sodium cyanide
Brain Teaser

• What chemical would you expect to find here?
  – Sodium perchlorate
  – Sodium hydroxide
  – Sodium cyanide
What’s Wrong Here?
What’s Wrong Here?

Oxidizer (30% Hydrogen peroxide) “stored in a flammable cabinet, next to Methanol

= Fire!
Open Discussion

• Let’s talk personal protective equipment (PPE)
  – What is required upon entering a lab
  – What PPE can be worn outside a lab

PPE includes:
• Safety glasses
• Closed toed shoes
• Lab coat
• Chemical gloves
HAZARDOUS MATERIAL LABELING
Globally Harmonized System

- OSHA has adopted a new labeling standard for containers and packages of hazardous materials
  - December 1, 2013 – training of employees in US
  - June 1, 2015 – new SDS and labels
HCS/GHS Labeling Components

PAINT (METHYL FLAMMALINE, LEAD CHROMOMIUM)

DANGER
Causes damage to the liver and kidneys through prolonged or repeated exposure to the skin.
Keep away from food and drink.
Wash hands thoroughly after use and before eating.
Highly flammable liquid and vapour.
Keep away from heat and ignition sources.

FIRST AID
Call emergency medical care.
Wash affected area of body thoroughly with soap and fresh water.

Great Lake Paints Inc., Columbus, Ohio, USA.
Telephone 999 999 9999

Pictograms
- Conveys specific information about the hazard(s) of a chemical

Product Identifier
- Chemical name or number to identify the chemical

Signal Word
- Alerts level of severity of hazard

Hazard Statement
- Describes the nature of hazard(s) associated with a chemical

Precautionary Statement
- Recommended measures to take to prevent adverse effects

First Aid Statement
- Emergency care information

Supplier Information
- Name, address and telephone number of the chemical manufacturer, importer or other responsible party
New GHS Hazard Symbols

- Many will look similar
  - Flammable
  - Oxidizer
  - Toxic
  - Corrosive
  - Harmful to the environment
GHS: Some New Symbols

- Respiratory sensitizer
- Mutagen
- Carcinogen
- Reproductive toxin
- Specific target organ toxicity
- Aspiration hazard

- Acute toxic (warning)
- Skin irritant
- Eye irritant
- Respiratory tract irritant
- Skin sensitizer
- Narcotic effects

- Gases under pressure
Labeling of Secondary Containers

Sample label - secondary container

Hazardous substances

Hazard Warnings
TIP! Clearly Identify a label station or drawer with words, such as: “Safety Labels”
Mini-Brain Teaser

- Which GHS label would you expect to find on a flammable liquid?
  - A

- Which GHS label would you expect to find on an irritant?
  - B
HAZARDOUS WASTE
Hazardous Waste Management

- **Characterize waste**
  - Corrosive (pH 2 to 12.5)
  - Flammable
  - Toxic
  - Reactive
- **Containerize**
- **Label**
- **Inspect**
- **Dispose within required time limit**
  - Typically every 90 days (for large producers)
  - But every 6 months for many businesses
- **Record keeping (manifests)**
- **Respond to spills**
- **Train**
Hazardous Waste Containers

- “Hazardous Waste” label
- Containers closed
- If a liquid, in a secondary tray
- Spills immediately cleaned up
- Inspected weekly
Hazardous Waste Labels

- Initial date of accumulation
- “Hazardous Waste”
- Composition (i.e., constituents)
- Physical state (solid, liquid, gas)
- Hazard warning statement
- Name and address of generator
Sharps

- Syringe with needle
- Scapels and lancets
- Razor blades
- Broken glass
Brain Teaser

- Which container(s) would you place an uncontaminated razor blade?
Brain Teaser

- The yellow or green container.
Brain Teaser

- If the sharps were contaminated with sodium azide which container would you place it in?
Brain Teaser

- If the sharps were contaminated with sodium azide which container would you place it in?
Universal Waste

- Are a type of hazardous waste
- Must be properly contained with a lid labeled as a Universal Waste
- 1 year accumulation time limit
- Examples include:
  - Batteries, cell phones, computers and computer monitors, electronic devices, fluorescent lamps, mercury wastes, non-empty aerosol cans, televisions
- You can not dispose of universal waste in the trash
Empty Containers

- Completely empty (no pourable liquid)
- Less than 5 gallons
- Must not have contained an ‘extremely hazardous substance’
- Do not triple rinse
- Write “EMPTY” on the label
- Dispose of in normal lab trash
Non-Hazardous Wastes

• Make sure to clearly label non-hazardous waste containers
  – Buffers
  – Treated biological liquid waste with no hazardous components (e.g., no sodium azide, no ethanol)
    • Properly treated with 10% bleach for 10 minutes
  – Green Non-Hazardous Waste
NO FLY ZONES
It is for Your Safety – Don’t Block

- Things that save you
  - Fire extinguishers
  - Eyewash stations
  - Safety showers
  - Fire alarm pull stations
  - Electrical panels
  - Exit paths
Electrical panels

DANGER

Area in front of this Electrical Panel must be kept clear for 36 inches. OSHA-NEC Regulations

Work Space Width
Section 110.26(A)(2)

Equipment 30 In. or Less

30 In. Wide

Equipment Over 30 In.

Width of Equipment

Working space in front of electrical equipment must not be less than 30 in. or the width of the equipment, whichever is greater.
Eye washes and safety showers
Eye washes and safety showers

Within 10 seconds. Best to have near fume hood. Need to be accessible (i.e., should not have to open a door to find it)
Fire extinguishers and fire pull stations
Fire extinguishers and fire pull stations

- Include location sign
- Install extinguishers between 3.5 and 5 feet above the ground
- Service annually
- Inspect monthly per OSHA and NFPA
- Many fire departments require 36 inch clearance in front and around fire extinguishers and fire pull stations
It is for Your Safety – Don’t Block

- Excess storage of chemicals.
- Exhaust slots blocked.
- Containers stored within six inches of face of hood.

Hood sash set above 18 inches.
Open Discussion

• Let’s talk food and drinks.
  – Do you allow food and drink in the same room as hazardous materials?
  – How are employees instructed on the requirements?
SELF INSPECTIONS
What hazards do you see?
Safety Training

Lab Safety Training

Compressed gas

Biohazards

Ergonomic
Safety Inspections

- Safety inspections include:
  - Observing work areas and operating conditions for general safety
  - Observing hazard communication policies (chemical labeling and storage)
  - Assuring equipment is operating properly
  - Assuring safety equipment has been inspected
**LABORATORY INSPECTION FORM**

To be completed quarterly. Retain for 3 years

<table>
<thead>
<tr>
<th>Department:</th>
<th>Inspector Name:</th>
<th>Date:</th>
</tr>
</thead>
</table>

Check all that apply. Follow up with problems that are found. Forward to Safety Committee.

### A. Hazardous Materials
1. Hazard Communication / Chemical Hygiene Plans available?
2. MSDSs are on file and readily accessible
3. Containers of stock solution are properly identified (e.g. buffers labeled and marked with words “buffer”)
4. Original product names (or full chemical names) and hazards (health/physical) are clearly identified on labels
5. Containers of nonhazardous substances are labeled explicitly to avoid confusion
6. Synthesized unnamed chemicals are labeled by their reactions and possible products and with probable hazards (health/physical)
7. Containers (bats/storage tanks) are labeled with contents
8. Visible piping is labeled with contents and direction flow
9. Designated area is established for the use of regulated carcinogens
10. Incompatible materials are segregated by chemical class
11. Infectious waste is properly labeled and placed in closable, leakproof containers/bags or puncture resistant holders.
12. Containers of materials are disposed of within manufacturer’s suggested expiration dates
13. Containers of peroxide forming chemicals are dated upon receipt and disposed of within manufacturer’s suggested expiration dates
14. Secondary containment is provided, as required, at the minimum for quantities greater than 55 gal., 500 lbs., or 200 ft.³
15. All chemical containers are closed, except when actively adding or removing material from them.
16. Chemicals are not disposed of by evaporation in a fume hood and/or into the room or atmosphere.
17. Are excess flammables located outside of a flammable cabinet?
18. Are all Class 1A flammables in non-breakable containers 1 pint or smaller?
19. Are all Class 1B flammables in non-breakable containers 1 liter or smaller?

### B. Compressed Gas Cylinders
1. Compressed gas cylinders are protected from external heat sources and stored in well protected, well vented, dry locations away from highly combustible materials.
2. Cylinder storage space will not be damaged by passing or falling objects and is not subject to tampering by unauthorized persons.
3. Cylinders are secured to structural component of the building with chains at 2/3 and 1/3 of the cylinder height.
4. Protective caps far in place while the cylinders are not in use or connected for use and valves are labeled “open” or “closed” when the cap is not in position.
5. Only cylinders with compatible substances are stored.

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**Inspections Are Fun!!**
Hierarchy of Controls

1. Eliminate
2. Substitute
3. Engineering Control
4. PPE
Tag Out

- Unsafe equipment must be tagged out
- Report unsafe equipment to a supervisor
What is Wrong Here?
Cleanup any spills right away

This must be managed as a hazardous waste
What is Wrong with this Hazardous Waste Container?
Hazardous Waste Containers must be labeled

Labels Require:
- “Hazardous Waste”
- Description
- Hazard(s)
- Accumulation start date
Best Practices

• **Periodic documented safety inspection** – at least quarterly
  – Promptly type up and assign action items with dates
  – Verify finding was corrected by next quarterly inspection at the latest

• **Make sure everyone on the team is wearing proper PPE**
  – Minimal safety glasses and closed toed shoes and possibly lab coat. Gloves if anyone touches anything

• **Include a team of preferably at least three people**

• **It is okay to include a non-lab person on the team - they often see things that you may miss.**
Summary

- Chemical inventory
- High hazard chemicals
- Chemical storage
- Chemical labeling - Globally Harmonized System
- Hazardous waste
- No fly zones
- Self inspections
Contact Information

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THE END