The Dionne Group

Safety Manual & Lab Regulations

October 2011

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Welcome!

Welcome to research in the Dionne Group! This manual is intended to give an overview of safety regulations in the lab, as well as highlight emergency procedures.

In addition to this manual, you should also refer to:

1. The "Quick-Start Guide for New Lab Members"
2. The safety presentations on "Chemical Safety," "Laser Safety," and "Compressed Gas and Cryogenic Safety." These are available online and in the blue laboratory safety plan binder, located in the Wet Lab.

Emergency Procedures

Fire & health-threatening hazardous material releases:
(includes all compressed gas cylinder leaks or valve failures)

1. Call 9-911

2. Activate fire alarm. Close door to lab or room

3. Evacuate area or building

4. Administer first aid

Chemical spill: remove clothing, deluge with water for at least 15 minutes, or until emergency personnel arrives

5. Notify Jen – 626-533-7922

6. Notify the safety officer (Ashwin)

Releases or incidents NOT immediately health-threatening

0. Contain or clean up the spill only if you are trained to do so. Otherwise,

1. Call 5-9999

24-hour EHS number to report chemical, radiation, and other health and safety incidents

2. Leave the area. Close door.

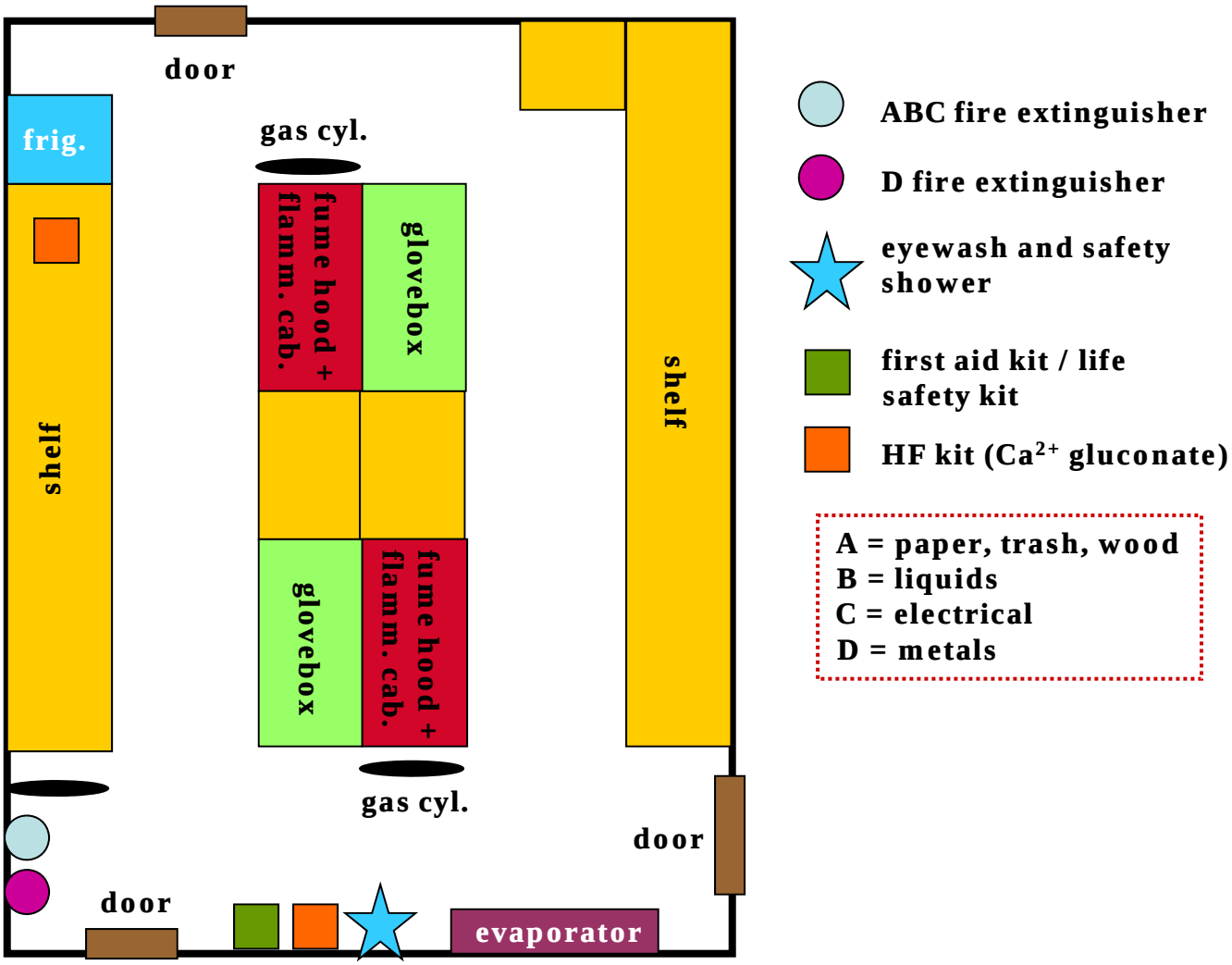
3. Notify Jen – 626-533-7922

4. Notify the safety officer

Non-Emergency Procedures

All incidents, large and small, must be reported to Jen & the safety officer (Ashwin)

ex: small extinguished fires, minor wounds, emergency equipment shutdown, small injuries that require first aid or a visit to Stanford Hospital or the Occupational Health Center, electrical hazards, small spills that can be cleaned up by the group, and any unsafe conditions.



Wet lab

Safety courses & training

All members *must* take the following safety classes:

- General safety and emergency preparedness (EHS-4200)
- Chemical safety for laboratories (EHS-1900)
- Compressed gas safety (EHS-2200)
- Laser safety (EHS-4820)

and, where applicable:

- Computer workstation ergonomics (EHS-3400)
- Laboratory ergonomics (call EHS at 723-0448)

Training must be documented in the "Laboratory Safety Plan" blue binder before beginning lab work.

Quarterly Safety Inspection

The safety manager will perform quarterly inspections of the lab space regarding i) general safety; ii) hazardous materials and waste; and iii) compressed gases.

This inspection ensures proper labeling and storage of chemicals, proper fume hood use (i.e., sash closed when not in use), proper gas cylinder storage, proper dewar storage, etc.

All lab members will familiarize themselves with the "Laboratory inspection checklist" and uphold practices that comply with the list.

‘In D Lab’: Commandments

1. Always wear safety goggles in the lab.

2. Wear lab-appropriate clothing, especially close-toed shoes.

3. Consult Jen or the safety officer before trying any new experiments or procedures.

4. Contain dangerous chemicals in the glovebox or hood.

5. Always leave the lab cleaner than you found it.

6. Label all waste and sample vials correctly.

7. Always transport chemical samples using a secondary closed container.

8. Ensure the safe condition of all lab areas before leaving the lab, especially at the end of the day.

9. Headphones and shiny/sharp jewelry are not allowed in the lab.

10. Volunteer for a group job!

Personal Protective Equipment

Safety glasses must be worn at all times upon entry into the wet lab. Please choose a pair that fit.

Shoes covering the feet are required.

Long pants must be worn in the laboratory.

The routine use of labcoats in the wetlab is highly encouraged; please replace them when they get dirty. Do not bring labcoats into the optics lab or office area.

Gloves must be worn at all times in the wet lab. Nitrile gloves are suited for resistance to solvents and organic chemicals, while latex gloves provide general resistance to acids and bases.* Change gloves when they become dirty. Remove gloves before exiting the wet lab.

* Special gloves (Neoprene, Silver shield) may be required for your work.

Instrument administrators

Please contact the following people for safety information and for instrument training, maintenance, and general questions:

Safety committee: Jen, Ashwin

Gloveboxes: Amr
UV-Vis-NIR: Hadiseh and Ashwin
Hood 1: Jon
Hood 2: Diane
Microscope & Spectrometer: Andrea and Sassan
Lasers: Jen
Evaporator: Brian
Simulation computers: Aitzol
Server: Amr

Instrument administrators are responsible for writing and maintaining standard operating procedures for their equipment.

Before starting an experiment

Practical safety considerations that accompany your experiment:

1. THINK!

a) What equipment do you need? Do you know how to use it?

- If you have not used a piece of equipment before, ask for a demonstration (or formal training if necessary), and have someone observe your technique before working on your own (e.g. Schlenk line, cryogen (LN_2) use, glovebox).

a) What chemicals will you use?

- Do you know how to safely handle them?
- Do you know how they might interact with one another? With the air? With water?
- Read MSDS for each chemical **and ask someone who has used it** about safety concerns. If no one in our group is familiar with the chemical, find someone in another group who is – DO NOT depend on the MSDS alone!

b) If you are unsure of any of the above, just ask. The locals are friendly ☺

Before starting an experiment

2. PLAN

a) Write down an experimental procedure, taking the above items into account.

b) Be sure to consider potential burn/spill/fire/explosion/corrosive hazards for your experiment.

- What extra personal protective equipment might you need? (The general lab requirements may not be enough.)
- Should you use a face shield? Do you know which type of fire extinguisher you would use and where to find it?

c) How will you clean up after your experiment?

- Will there be toxic waste/byproducts that need to be disposed of?
- How will you clean/prepare the equipment to ensure it will be safe for the next user?

Before starting an experiment

3. GET A SECOND OPINION:

a) Make sure you **ask someone to review your plan** and see if there are any safety hazards that have not been considered. This is necessary at any experience level.

b) The less familiar you are with the materials/techniques you are using:

- the more senior the colleague you should speak with,
- the more detail you should provide,
- the more detailed questions he/she should ask you about your plan.

If the experiment you have not performed previously involves any of the following, you must review it with at least two lab members (preferably including a lab safety officer) before proceeding:

i) **Pyrophores**: ex. $ZnMe_2$, $CdMe_2$, $AlMe_3$, alkyllithium, Grignards

ii) **Toxic chemicals**: i.e., organometallics; heavy TM and main group metals: Cd, Te, Pb, Se, As, Co, Hg; silanes

iii) **Oxidizers:** peroxides, permanganates, perchlorates, piranha

iv) **Strong reductants:** Na, Li, K, etc.

v) **Corrosives**: *aqua regia*, piranha, nitric acid

vi) **High temperature**: T > 200 °C

vii) **Large volume reaction (> 250mL)**

viii) **IR, UV, or Pulsed lasers**

Before starting an experiment

4. PERFORM YOUR EXPERIMENT:

a) Even the best laid plans can have problems. Make sure to pay close attention to what you are doing while you work.

- Avoid distractions (no headphones).
- Be prepared for potential problems (even non-safety problems that occur may cause you to rush to correct them, thereby causing an unsafe situation).
- It is best to work with others in the general area, in case there is a major unforeseen problem. Be extra cautious if this is not possible. It may be best to wait if your experiment is particularly unfamiliar and/or dangerous.

5. THINK!

a) Have you cleaned up chemical and materials waste (pipets, vials, etc.)?

- In the glovebox? At the balances? Other common areas?
- At your bench/hood/wherever your experiment was performed?
- If not, you may have contaminated your labmates' experiments.
- Pay attention to sharps disposal, so labmates do not cut/stab themselves.

b) Have you cleaned/prepared any equipment for the next user?

- Turned off hotplates?
- Turned off vacuum pumps and/or gas cylinders if necessary?

Chemical Waste I

LIQUID WASTE

EHS will provide containers for liquid waste. Please:

1. Keep aqueous and organic waste separated.
2. Label waste containers with contents. Use pencil.
3. Estimate percentage of components.
4. Keep lid of waste capped with pressure-release top when not in use.
5. Do not overfill liquid waste containers.
6. Submit a pickup request when waste is full, or before 8 months: *wastepickup.stanford.edu*

VOLATILE WASTE

Please do not dispose of volatile waste directly into the contaminated waste buckets. Quench material if needed and allow it to evaporate in the fume hood before moving to the open lab environment.

e.g.: Kimwipes saturated with solvent, pipets with odorous chemicals (i.e., thiols)

Chemical Waste II

SOLID WASTE

There are both trash cans and contaminated waste containers in the lab. Please dispose of non-contaminated materials in the trash bins (handled by custodial staff without PPE).

Chemical waste (gloves, used vials, pipets, syringes) is collected with PPE by EHS.

SHARPS

DO NOT dispose of sharps in either the liquid waste or the contaminated solid waste buckets:

* needles (do not recap needles)
* razor blades

Please use a designated sharps container (one in each hood)

HAZARDOUS WASTE

All laboratory chemical waste must be managed as hazardous waste unless it is listed on the SU non-hazardous waste list (*nonhazardouswaste.stanford.edu*)

Chemical Waste III

USED BATTERIES

Used batteries cannot be collected in labs. Please bring your used batteries to the nearest battery recycling center (*batterybuckets.stanford.edu*) or contact Chris Craig at ccraig@stanford.edu

FLUORESCENT & UV LAMPS

These items are universal waste and cannot be thrown into the regular trash or broken glass boxes. Place in a hard-sided contained, label with "universal waste," identify what the contents are, and indicate the date. For disposal, contact the facilities manager.

Gases & Cryogens

CYLINDERS

Gas cylinders should always be fixed to the wall with the chain holders when in use and when stored.

DO NOT move a cylinder when it is uncapped or with the regulator attached.

Ensure that you have the proper regulator for the gas you need (i.e., Ar, H_2).

Please use a cart when transporting cylinders.

DO NOT let the glovebox Ar cylinders run empty, and only use the high purity Ar.

CRYOGENS (i.e., dry ice, LN_2, LHe)

Please use with proper ventilation and handling. Dewars must be restrained at one point. If you have never used a cold trap with a vacuum manifold, please ask the safety team (Jen, Sassan, Ashwin) for help.

Schlenk Line Safety

New group members and inexperienced users should always seek assistance before using.

Working with Vacuum:

Use appropriate sturdy, tubing.

Check for cracks in glassware before using vacuum.

Keep sash low to protect from implosion and when not in use.

Do not perturb glassware while under vacuum.

Vent vacuum line BEFORE removing dewar to a liquid nitrogen trap to prevent catastrophic expansion of condensed gases.

Liquid oxygen is highly reactive and dangerous! If you remove your dewar and find a blue liquid in your trap, IMMEDIATELY replace the dewar, close your sash, step away and warn others.

Working with Inert Gas:

Protect against pressure build-ups by ALWAYS connecting an opened pressure relief bubbler to any reaction, purging system or system being heated. Leave the bubbler open to dissipate pressure even if the gas supply is closed.

When switching to vacuum, close the gas flow to a reaction BEFORE closing the bubbler.

Secure all connections or septa with clips or wire, and use clips that are appropriate for your temperatures.

Never have openings facing your body so that if a septum pops, chemicals will not be sprayed at you.

Glovebox Safety

Manuals, including purging instructions, are located on the tops of the gloveboxes.

SAFETY

1. Put a sign on the glovebox when hotplate is on or hot.

2. Minimize contamination: Quench materials which have touched pyrophoric chemicals ($CdMe_2$, $ZnEt_2$, TBP, $TiCl_4$, etc.) with an alcohol (MeOH or IPA), then purge. Rinse thiol-containing compounds (like HDMS) with MeOH, then purge.

3. Prevent glovebox holes by being smart with sharps: use dust-busters to clear broken pipette shards, keep caps on needles, and don't stuff too many pipettes in or out.

4. Prevent spills: close solvent bottles, use a vial holder, keep a new piece of Al foil under work space to keep glovebox floor clean. If you spill, clean it up with Kimwipes and purge the glovebox.

Glovebox Citizenship

1. Wear a pair of latex gloves over the glove-box gloves, to keep the glovebox gloves relatively new and contamination-free.

2. Please keep the glovebox clean: do not leave any used items on the glovebox floor (i.e., used foil, used gloves, used pipets). Also, be sure to label and store all vials. Do not leave samples sitting out for extended periods of time.

3. Properly introduce materials in to the glovebox with adequate pumping in the antechambers (3x Ar/vacuum cycles).

3. Keep Ar cylinders ≥ 200psi. Change the cylinder when at ~300 psi.

4. Sign the logbook with name, date, time, and material before you go in. When done, record pressures of H_2O, O_2, Ar, end time, and other notable occurrences.

5. Report any concerns to the glovebox guru or Jen.

Chemical Handling I

Pyrophores

Ex: $ZnEt_2$, $CdMe_2$, $AlMe_3$, alkyllithium, Grignard reagents

Hazards: A pyrophoric substance will ignite spontaneously; that is, its autoignition temperature is below room temperature. Pyrophoric materials are often water reactive as well, and will ignite when they contact water or humid air.

Handling: Pyrophoric materials can be handled safely in atmospheres of argon or (with few exceptions) nitrogen. Most pyrophoric fires should be extinguished with a Class D fire extinguisher for burning metals.

Disposal: Small amounts of pyrophoric materials and empty containers must be disposed of carefully, by quenching the residue. Less reactive substances can be disposed of by diluting heavily with an unreactive solvent like hexane, placing the container in a cooling bath, and adding water dropwise. More reactive substances can be quenched by slowly adding the dilute solution to dry ice, then adding a mildly reactive substance, which does not freeze in dry ice, to the mixture (wet diethyl ether, acetone, isopropyl alcohol, and methanol are often used).

All of these reagents will react vigorously with protic solvents, alcohols to produce alkanes or hydrogen. $M(CO)_n$ may not be so reactive. You should be extremely cautious when disposing of these extremely pyrophoric chemicals! Large volumes should only be handled by someone with experience.

Chemical Handling II

Corrosive Solutions

Ex: nitric acid, "piranha" (conc. H_2SO_4 : 30% H_2O_2, 3:1 v/v), *aqua regia* (HNO_3 : HCl, 1:3 v/v)

Hazards: All of these chemicals are very powerful oxidants which form explosive mixtures with organic compounds. Mixing piranha is highly exothermic, and the solution will boil. Beware of outgas products of both piranha and *aqua regia*.

Handling: These solutions should never be prepared in large amounts (i.e., >100 mL), and should not be stored for future use. These chemicals are one of the most common causes of explosion in inorganic chemistry laboratories.

Disposal: All of these solutions should be diluted 100-fold before putting into a labeled waste container.

Handling *aqua regia*:

1. Use a reagent that is milder than *aqua regia* for cleaning glassware if it will suffice.
2. Do not take *aqua regia* out of the fume hood in which it was prepared, and do not store it there either; make only what you need and destroy the residue. *Aqua regia* can be destroyed by cautious and careful dilution with water; talk to the safety officer for a detailed procedure. If necessary, the solution can then be neutralized and disposed of in the approved manner.
3. Never put *aqua regia* in a closed container.

Chemical Handling III

Heavy Main Group Elements

Ex: Ga, In, Tl, Ge, Sn, Pb, As, Sb, S, Se, Te, Po

Hazards: Organo-derivatives of these compounds should be avoided and otherwise treated with extreme caution: $Me_3Si\text{-}S\text{-}SiMe_3$, $Me_3Si\text{-}Se\text{-}SiMe_3$, $Me_3Si\text{-}Te\text{-}SiMe_3$, $(Me_3Si)_3P$, $(Me_3Si)_3As$ are very reactive and will liberate H_2S, H_2Se, H_2Te, PH_3, AsH_3. These are all **EXTREMELY TOXIC** gaseous compounds.

Handling and Disposal: All of these compounds should be handled in the glovebox and quenched with methanol. The atmosphere should be purged before opening the antechamber door.

Cadmium Oxide (CdO)

Handling and Disposal: Cadmium oxide should be handled in the gloveboxes and not on the laboratory bench. Any spilled materials should be thoroughly cleaned up. CdO should be rinsed into a waste container that is labeled as containing cadmium.

Chemical Handling IV

Metal Carbonyls (& Gas Liberators)

Ex: **$CdMe_2$, $Fe(CO)_5$, $Co_2(CO)_8$, $Zn(Et)_2$**

Hazards: Dangerous! Metal carbonyls are coordination complexes of transition metals with carbon monoxide. Metal carbonyls are toxic, in part because of their ability to carbonylate hemoglobin to give carboxyhemoglobin, which will not bind O_2.

Handling dimethylcadmium: Quench $CdMe_2$, including all glassware, pipets, etc. with alcohols in the glovebox after you have closed the stock container. All subsequent equipment (syringes, etc.) that comes in contact with $CdMe_2$ should be thoroughly rinsed with alcohols before disposal. There are special silver lined gloves that are essentially impermeable to dimethylcadmium, though a little cumbersome. PVC AND LATEX GLOVES SHOULD NEVER BE USED TO HANDLE TOXIC CHEMICALS. Nitrile gloves are less permeable and offer better protection.

Chemical Handling V

Peroxidizable Compounds

Examples: Peroxide-forming substances include: aldehydes, ethers (especially cyclic ethers), compounds containing benzylic hydrogen atoms, compounds containing the allylic structure (including most alkenes), vinyl and vinylidine compounds.

Hazards: Capable of reacting with atmospheric oxygen to form potentially explosive peroxides. Formation of peroxides is accelerated by light and heat. Substances which have undergone peroxidation are sensitive to thermal or mechanical shock and may explode violently.

Handling: Labels on peroxide forming substances must contain the date the container was received, first opened and the initials of the person who first opened the container, including a notice such as "Warning: Peroxide Former" on the container. They should be checked for the presence of peroxides before using, and quarterly while in storage. If peroxides are found, the material should be decontaminated or disposed of. The results of any testing must be placed on the container label. If the peroxide forming substances has been opened and more than one year has passed the material should be discarded. Do not treat any peroxide-forming chemicals if you are unsure of the age, there are visible crystals, or a precipitate or oily viscous layer is present. Never distill substances contaminated with peroxides. Never use a metal spatula with peroxides. Contamination by metals can lead to explosive decompositions. Store peroxides and peroxide forming compounds at the lowest possible temperature, away from light and heat. If you use a refrigerator, make sure it is appropriately designed for the storage of flammable substances.

Optics Lab Safety

New Laser / Optics Lab Users:

1) Sign up for laser safety training.
2) Contact the group laser safety officer before using a laser.
3) After training by the group guru, indicate completed training in the blue safety binder.
4) Be sure to keep the optics lab inventory (in google docs) up-to-date, whenever new equipment arrives or equipment is borrowed/loaned-out.

Laser Use Regulations:

1) You must be an authorized laser user to work with lasers.
2) **Protect yourself**:
    - Wear safety goggles when there is the possibility for exposure above the maximum permissible exposure (MPE) for your laser.
    - Remove shiny jewelry (especially rings or watches) during laser use.
    - Perform regular stray beam
3) **Protect your colleagues**:
    - Ensure proper signage is posted when laser is in use.
    - Close curtains around door when laser is on.

Non-Laser Users:

Obey hallway laser signs. It's a good idea to knock when entering the optics lab even if a "laser in use" sign is not on.

Medical attention CAN mitigate the effects of laser exposure if provided promptly. In case of an emergency, call 9-911 from a campus phone.