

Laboratory safety -LSCI

Safety first! Everyone working in the lab must first consult the EPFL's *Rules of Hygiene, Safety and Environmental Protection*. Below are some summaries of this booklet.

1. 1. General considerations.

1.1.1. Each group member (Ph.D., Postdoc, visiting scholar) need to get a safety training from EPFL. If you are not notified by the safety office of EPFL for this training, please ask your safety delegate how to sign up for the training.

1.1.2. Lab goggles/safety glasses must be worn at all times while inside the lab. This is extremely important because even things seem pretty common and safe (e.g., using the rotovap, placing glassware under reduced pressure) can lead to accidents. Furthermore, it is hard to foresee the danger of other people's lab manipulation while you are in the same room, and thus safety precautions need to be taken. This applies also to those who wear normal eyeglasses – you need to wear a pair of goggles/safety glasses on top of it.

1.1.3. Do not wear your lab coat or your gloves at your desk, or any office area. This includes common areas, such as at the computers of the NMR, or the GC machines. Never wear a lab coat outside the wing our labs are located: keep in mind that you cross public spaces where people are unprotected as you go from your lab to the chemical shop, or the HRMS room.

1.1.4. Do not wash your gloves with organic solvents (Latex or nitrile gloves are permeable to acetone, for instance). More information on gloves, see page 12 of the safety booklet of EPFL.

1.1.5. Know where safety showers and eye washes are located. Know how to use them. Consult your safety officer if needed.

1.1.6. Know where the fire extinguishers are located. Know how to use them. Consult your safety officer if needed.

1.1.7. Not to work alone, especially if you are doing chemistry of sensitive compounds outside of the glovebox. This does not include office work in isolated area.

1.1.8. Check the MSDS or other safety information for each chemical you are working, if it is your first time working with that chemical, or if you have specific concerns. Consider if hazardous waste products may be formed and plan beforehand how to deal with them.

1.1.9. The window of the fume hood is must be kept closed as soon as the need of access to it is over

1.2. Acquisition, storage, and transportation of chemicals.

All the other chemicals should be stored according to the hazard group. All chemicals should be properly inventoried. All the chemicals are shared by all people in the lab.

1.3. Use of chemicals

Highlights:

- Each coworker must have access to the material safety data sheets of his (her) own commercial products and must know how to read it.
- It is forbidden to use simultaneously a workplace for storage and for an experiment. (Example: a fume hood cannot be a storage place and a place for synthesis).
- The use of carbon tetrachloride is forbidden. The use of benzene requires an authorization if no other solvent can replace it.
- No more than 100 litres can be stored by laboratory (including wastes) in ventilated safety cabinet. Bring your waste downstairs regularly.
- In general we don't use alkali metals and their alloys. Inform Hu if you need to use them. A small reserve is available at the chemical shop.
- **Hydrides, silanes, phosphorus, phosphines, nickel Raney, platinum on carbon** and other spontaneously flammable compounds are stocked under inert atmosphere or appropriate liquid. **Avoid triethoxysilane.**
- **A rule of thumb is that when you use potentially explosive/flammable chemicals, use a small quantity (mg scale). Don't try large reactions before you discuss with HU.**
- All chemical reactions must be performed under a hood, even when considered harmless.
- **When you work with explosive/flammable chemicals, high pressure gas, etc, don't work alone. Get a group member to be ready to help!**

Common Explosion Hazards

1. Oxidants in combination with organics can lead to violent exotherms/explosions. Before disposing of large amounts, think of what it may react with and when in doubt place in a separate waste container. Oxidants (e.g., bleach, Cr^{VI} and Mn^{VII} salts, hypervalent iodine reagents, H₂O₂, etc) should be placed in separate waste from organic reagents/solvents. **H₂O₂ explodes when it is dried. Only use in H₂O₂ in water; never try to evaporate a reaction mixture in contact with H₂O₂.**

2. Oxidizing acids (e.g., nitric acid and aqua regia) can react extremely violently with organics (especially acetone), and the resulting explosions/release of corrosive solutions can lead to serious injury. Acids should always be stored in a **separate location** from organic chemicals. Additionally, waste bottles for acids should be clearly marked and placed in a **separate location** from organic waste. This will prevent mistakenly pouring acid waste in with organics (which is the most common cause of this type of explosion). **Aqua regia should not be used by students who have not be trained by the group safety officers on proper precautions for usage and disposal.**

3. Perchlorate salts can explode without warning, especially when concentrated in the presence of organics (once again, ClO_4 is a strong oxidant!). Always use a blast shield when concentrating mixtures containing these salts and **avoid the use of the ClO_4 counter anion** whenever possible.

4. Metallic lithium/Al/Cs should **never** be placed in N_2 filled dry boxes or under a nitrogen atmosphere on your line. A violent and highly exothermic reaction will result from spontaneous " Li_3N " formation.

5. Remember that something as common as flash chromatography columns are run under high pressure and can crack/explode unexpectedly.

6. The condensation of liquid O_2 , liquid N_2 and solid Ar in traps on your vacuum line can lead to explosions. See the vacuum line safety section for further details.

7. **Be careful with azides and diazo compounds.** Azides can explode under turbulence. When you collect azides from a frit, do not scratch the wall or bottom of the frit to get more products. Scratching may lead to explosion. If you have to work with azides, use small amounts. Never heat an azide unless it is dissolved in solution. Be careful not to let all the solvent evaporate. Do not heat to high temperature.

NaN_3 is not compatible with certain heavy metals; It reacts with acid to form hydrazoic acid. Be careful.

NaN_3 reacts with halogenated solvents to form explosive diazomethane. Never use NaN_3 in chlorinated solvents.

Let HU know if you need to work with azides or diazo compounds.

8. **Be careful with tert-BuLi.** Avoid it if you can. If you cannot, let HU know before you use it. In principle, you can only use it in the glove box. Tert-BuLi burns violently when encountering air. **Do not use tert-BuLi in THF and ether. It burns.**

9. Pyrolytic materials: follow recommendation of Aldrich Bulletin Al-134 (also on our website, the research page).

10. **Pd and Ni over Carbon catalysts** are known to be flammable. So it is normal if one sees fire when working reaction up. This is probably why some people use Pd/C that contains water. Water is compatible with this catalyst. So when you do hydrogenation reaction using Pd/C, be cautious. Pd/C with methanol is a dangerous combination, so should be avoided. With EtOH might be work. In any case, make sure you are aware of the danger and be ready for any small fire. In particular, work in the hood where there are no other flammable materials nearby (such as solvents, reagents). Have quick access to water to put out a small fire.

Toxicity Hazards

- Thallium salts (e.g., TlOEt).

- Alkyl mercury salts (e.g., HgMe₂). **Warning: never use HgMe₂ or similar organoHg compounds.**
- Tin reagents (especially tetra-alkyl or tri-alkyl aryl Sn compounds).
- Alkylating agents (e.g., MeI).
- Be careful with sulfur containing molecules as they can be quite smelly! **Never use thioacetone!**

I. Exercise extreme caution when using these reagents!! Clean up spills in your hood and in public areas (balances, dry boxes, etc) immediately using appropriate procedures, and dispose of cleaning supplies/gloves in solid waste containers beneath the hood (to avoid fume inhalation).

II. (i) dispose of all contaminated waste in a separate Ziploc bag before removing it from the box, and (ii) purge the box after the use of these compounds (and before opening the antechamber).

1.4 Forbidden unattended experiments

- It is forbidden to leave unattended an experiment if :

- use of toxic gas, like CO, phosgene, phosphines, chlorine
- very exothermic reaction as diazotation, Grignard, hydrogenation, nitration, etc.
- manipulation of alkali metals.
- prepare a reaction in autoclave.
- manipulation of flammable solvents in opened system.

1.5. Authorized unattended experiments

For routine reflex overnights, a note describing the experiments and safety measures should be taken, e.g., in a hood with automated fire monitoring system, and/or with a double safety system a) a probe linked with the apparatus, b) an independent probe which cuts power in case of troubles. We use an oil bath or IKEA heat block for heating. **The heating mantels are forbidden.** Please ask your safety delegate if you have questions.

1.6. WASTE DISPOSAL AND TREATMENT

There are strict rules at EPFL for waste disposal and treatment. See section 4 of the EPFL safety booklet (pages 8) for rules.

As a rule of thumb, nothing goes into the sink except for aqueous solutions containing less than 5% of organic (including acetone but not ethanol or sugar), and without heavy metal or toxic matters.

1.6.1. Disposal of Pyrophoric Materials

1.6.1.1 Pyrophoric materials from commercial sources (e.g, alkyl lithium reagents, Grignard reagents) that are still in their bottles can be given to chemistry waste disposal without quenching if they are still in their bottles. This is the safest way to dispose of these reagents.

1.6.1.2. Collect small amounts of pyrophoric metal or metal alloys (Na, K) in the box.

If you are quenching a very small amount of pyrophoric materials before disposal, you should do so with EXTREME caution! Remember that one mistake can be catastrophic and literally burn down the lab and injure a large number of your colleagues (and yourself!). The following general procedure should be followed – WHEN IN DOUBT CONSULT HU – before doing anything like this!

- a) **Locate the appropriate fire extinguisher in the lab before starting this procedure and be sure that you know how to use it. Do not be complacent.** Fires can result even if you have done the same procedure 99 times before. **PLEASE NOTE THAT A SPECIAL FIRE EXTINGUISHER IS REQUIRED FOR FIRES INVOLVING PYROPHORIC MATERIALS!! Know the proper fire extinguisher – this could literally be a matter of life and death!** Don't be hesitant to ask a colleague to stand by with the fire extinguisher as you are performing the quenching. In case of an accident, someone standing by 2 meters away, but fully focused on the current situation will be able to react more adequately than someone who is directly impacted by it. Make sure people in your lab who are not directly involved know what you are doing, to minimize any panic reactions, should anything go wrong.
- b) Clear your hood **and the area around it** of all flammable solvents (wash bottles, flasks containing solvent, solvent bottles, etc). These can catch on fire very easily and turn a small containable fire into an extremely dangerous fire.
- c) Clear your hood and **the area around it** of any paper materials – this includes Kimwipes, paper towels, etc. Again, these can catch fire easily and turn a small fire into an uncontrollable one.
- d) Place the flask containing the material to be quenched into a secondary container. This is important because if your flask breaks (which can easily happen from vigorous stirring) the pyrophoric material will be contained.
- e) Suspend the pyrophoric material in hexanes/toluene or some other inert solvent if there is not solvent in there already.
- f) Fit the flask with a **large** reflux condenser (and put the N₂ inlet on the top of this). This serves two purposes – (i) it provides additional headspace for when H₂ gas is generated in the quenching process and (ii) limits exotherms in the quenching process by allowing for the solvent to reflux (thereby cooling the mixture).
- g) Fit the condenser on the flask containing the material to be quenched with a N₂ inlet and a vent. An N₂ atmosphere is important for safely quenching these materials because fires are caused by the highly exothermic reaction of H₂ with O₂ in the presence of heat and a flammable solvent. Without O₂ a fire is unlikely – although dangerous exotherms can occur which can explode your flask and/or make the pyrophoric materials shoot out uncontrollably, so be sure to have adequate ventilation and **ADD THE QUENCHING AGENT EXTREMELY SLOWLY!!!**
- h) Add MeOH to this mixture **SLOWLY** over the course of hours/days. When in doubt about the proper rate of addition, go slower. Alternatively, cool the mixture to be quenched on dry ice batch.
- i) Keep in mind that metals (Na, K, Na/K) get an oxide coating around them in the quenching process. As a result, there may still be some metal present even after several hours/days stirring in the presence of MeOH. After several days, it is usually safe to add H₂O slowly to quench the final material. But again, use caution – and do not do this until there are not noticeable large chunks of metal present.

1.7. In case of accident or solvent spill

FOR ANY CASE OF EMERGENCY CALL 115

- While calling to the rescuers, indicate:
- The place where the victim is.
- The room number where the victim is.
- The phone number where one can contact a person staying near the victim.
- The persons close to the event assist the rescuers.

For medium or large solvent spill, use the emergency kit (mineral absorbent) which allows to collect the solvent spill on the ground. See the EPFL safety booklet.