Laboratory of Inorganic Synthesis and Catalysis
Ecole Polytechnique Fédérale de Lausanne

Lab Manual

Guidelines, Procedures, & Requirements

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Introduction

This manual contains the general guidelines for the research activities in our lab. **A perspective lab member should agree to follow this manual before deciding to join the lab**. In particular, every lab member needs to follow strictly the **safety** practices, as stated in the EPFL safety guidelines, and this manual. **Group job** descriptions and assignments are included, and will be updated periodically. Guidelines for the reading of **literature** and the writing of lab **notebook** and **publication** are outlined. Protocols for the use of **Schlenk lines**, **glove boxes**, cleaning of **labwares** are described. Procedures for the use of lab and institutional **facilities**, such as solvent purification system, IR, UV-Vis, NMR, GC-MS, GC, MS, X-Ray, Elemental Analysis, are presented.

Philosophy

The research in my group is expected to be **TEAM WORK** oriented. Each member of the group will get to work on her/his separate and independent project. Additionally, each researcher is supposed to contribute their individual abilities to help the other members of the group to successfully accomplish their goals or gain new skills. This way we are hoping to work as a highly competitive group in our field of research and to build lasting friendships among the members of the research team.

First law of research: how much you put in your work is how much you get out!
Third law of research: those who help always get the help from others!

Administration

- At EPFL and Switzerland, a contract can be terminated anytime within the first 3 months of your arrival. Keep in mind that you will be evaluated during this grace period, on whether you can execute safe and competent practices in the lab.
- Any new lab member need to get safety training from EPFL. Find out how you can do it from our safety officer or from HU.
- Please notify HU if you will not be in the lab for more than 4 hours during working hours for any reasons.
- Please notify HU if you cannot attend a group meeting for any reason.
- Please notify HU at least 2 weeks in advance for any of your vacation plans. Exception may be granted in a case-by-case scenario.
- Please notify HU for any ordering. Keep a record of what you have ordered and what have arrived in excel format. Search different suppliers to obtain the most economical resources.
- All chemicals and glassware are shared within the group.
- Please notify HU if you want to submit samples to institutional services (except NMR).

Additional points for Ph.D. students

- Make sure you keep track of the requirements of the doctoral school. Know when you need to submit your progress report, have your qualify exam, etc. Ask Anne Lene if you have questions.
- Your initial contract is one-year and it is subject to annual renewal. In the 9th month of your first year, a decision will be made whether to continue supporting your study. You will be evaluated against your potential of receiving a Ph.D. from EPFL. The academic performance of senior Ph.D. students in the lab can serve as a reference.
- Consult HU before you enroll in any class.
- Keep track of your teaching credits.
- Learn a bit of French so you may TA francophone undergraduates after 2 years.

Description of Lab Jobs

The following group jobs are assigned to one or two specific member(s) of the group.

Safety Officer: Monitor lab activity and take appropriate actions to comply the safety regulations. Organize the lab for safety visits. Monitor the waste collection and disposal process. Monitor the time that waste is in your personal area so that it is not there longer than the maximum allowable time. Answer the questions raised by the other group members in terms of safety training and practice.

Solvent System: For the person in charge, train new lab member and reload the solvents. For every user, always record use, notify those in charge of system if tanks are low, monitor gas level, and use good practice by following solvent system manual located next to apparatus.

Chemical Inventory: Make sure the inventory is up to date. Inform new lab members how it works. Store all public labwares and chemicals.

Rotary Evaporator: Maintain rotovap and area and keep all glassware associated with the rotovap safe. Train new lab members

GC: Maintain the instrument and train new lab members. Keep the area clean.

FTIR, IR Cells: Maintain IR and cells, train new lab members. Keep the area clean.

Electrochemistry Equipment: Maintain the instrument and train new lab members. Keep the area clean.

UV-vis and Cells, fiber optics: UV-vis area is kept neat and UV-vis is kept working.

Photolyzer: Maintain the instrument and train new lab members.

Cafeteria: Defrost and clean out fridge every 3 months. Clean the coffee machine every 2 weeks. Maintain the cafeteria area.

Printers: Keep printers functional. Replace cartridge when it runs out.

High pressure NMR: Maintain setup for high pressure NMR. Train new users in the group.

Liquid nitrogen refill (every Monday)

Green Glovebox

Parallel synthsizer

The following group jobs are assigned to everyone who uses the corresponding equipments.

Dry Boxes: Regenerate once the O_2 or H_2O level is too high (O_2 > 3 ppm, H_2O >5 ppm) or every 6 month. Check and change the regeneration gas tank after use. Change pump oil after each regeneration. Check gloves periodically.

Hoods: Police the hood areas to keep clean and check the fume hood survey card periodically to make sure they do not need to be serviced or inspected.

Balances: Check on and keep area clean near all balances, calibrate when necessary, and make sure they are always balances using bubble meter on the machine itself.

Base Baths: Clean and refill base baths periodically (as needed). Ask a senior lab member for refill procedure if unclear.

Ovens: Label any glassware going in to the oven with your initials and try to keep oven use to a minimum.

Computers: Keep computer updated and functional.

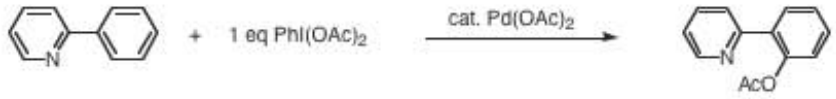
Lab Protocols I: Reading, Writing, and Presenting

I-1. Lab Notebooks

1.1. Maintaining a clear, well organized, and up-to-date lab notebook is critical for (a) keeping track of our experiments for your thesis, (b) any publications/ patents that you will write and (c) enabling future generations of students to reproduce your work.
1.2. General instructions for keeping a lab notebook are as follows.
1.3. Use only non-erasable ink in your notebook.
1.5. Write the reaction/experiment clearly at the top of each page. If you are following a published procedure, indicate the reference from which the procedure was obtained.
1.6. Make a table including each reagent, its molecular weight, the measured quantity – g (or mL), mol, and eq – used in the reaction, and the commercial source/purity of the reagent.
1.7. Write a detailed experimental, including the rate/order/time/temperature of addition of each reagent and solvent, and, where appropriate, any color changes that take place during the reaction. Also, detail all work up procedures and TLC data (where appropriate) for the reaction.
1.8. Be sure to weigh the product and determine the % yield for all reactions!!
1.9. Sample name for NMR/IR/GC/GC-MS/X-ray/Elemental Analysis etc should be always the same. It should be labeled according to the notebook number, page, and sample they refer to. For example, xhu10124 would refer to Xile Hu notebook #1, p. 12, sample #4.
1.10. Everyone is responsible for backing up their data on Zip disks or CD's.
1.11. A sample lab notebook page is shown below.

Sample Notebook Page

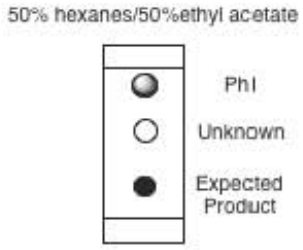
Date: 9/14/2004



Chemical	Source	Mol. Weight	mmol (Eq)	Amount
$Pd(OAc)_2$	Pressure	224 g/mol	0.064 (0.05 eq)	14 mg
2-phenylpyridine	Aldrich	155.20 g/mol	1.29 (1 eq)	200 mg
$PhI(OAc)_2$	Acros	322.10 g/mol	1.29 (1 eq)	415 mg
AcOH (solvent)	Fisher			8 mL

Reference (if applicable)
Procedure
• Pd(OAc)2, PhI(OAc)2 and 8-methylquinoline were placed in a 20 mL vial in that order. Acetic acid (8 mL) was added. Mixture is a clear suspension with yellow solids at bottom of vial.
• Placed in oil bath at 100ºC and heated for 1 hr. After 5 min, color changes to black.

• Removed vial from bath and allowed to stand at 5 min at room temperature. Opened and removed ~10 mL for GC analysis.
• GC (GC1, mss short method) shows 8% starting material (retention time 4 min) and 80% of a new peak at 6 min. Other unidentified peaks were observed at 7 and 9 min (5% each). **GC labeled xhu10124**. (Notebook 1, page 012, 4th sample)
• Rotovapped vial to dryness. Some of the material bumped into the rotovap trap. Recovered material by rinsing the trap with acetone (3 x 5 mL). Some remained stuck in the rotovap trap.
• Dissolved reaction mixture in methylene chloride. Ran TLC's in 40%/60% and 50%/50% and 60%/40%hexanes/ethyl acetate. Optimal conditions were 50%/50% hexanes/ethyl acetate (product rf ~ 0.2).



• Mistakenly dropped vial on bench and spilled approximately 1/4 of material. Yield is expected to be low as a result.
• Rotovapped to dryness and redissolved in 50% hexanes/50% ethyl acetate
• Loaded onto silica column (50 g silica, wet-packed in 50%/50% hexanes/ethyl acetate), and collected 100 fractions. Every other fraction was TLCed and fractions 7-9, 11-14, and 32-47 (each of the three spots were collected and rotovapped to dryness. Obtained 114 mg of fractions 7-9, 10 mg of fractions 11-14 and 212 mg of fractions 32-47.
• GC's of each set of fractions were obtained: Fractions 7-9: mss27.002; Fractions 11-14: 1mss27.003; and Fractions 32-47: 1mss27.004. Each appears to be pure.
• 1H NMR spectra of each fraction was obtained in CHCl3. Fractions 7-9: **xhu10124_1**; Fractions 11-14: **xhu10124_2**; and Fractions 32-47: **xhu10124_3**.
Conclusions from 1H NMR and GC analysis:
Fractions 7-9 are iodobenzene with some other solvent impurities.
Fractions 11-14 contain aromatic and aliphatic peaks. Need to do more analysis to figure out what this is.
Fractions 32-47 are the expected product. No solvent is present.
Molecular weight of product: 213.2 g/mol
Amount Expected: 275 mg
Amount Obtained: 212 mg
% Yield: 77% yield

Another reference to the writing of lab notebook can be found at:
http://ccc.chem.pitt.edu/wipf/GLPs.html

I-2. Literature reading

It is important to keep up on the current literature in your field, particularly as it relates to your project. Note that reading the literature is critical not only to learn more about your project/area of research but also to get you prepared for upcoming seminar speakers, proposal writing, orals, local and national and international conferences, writing your own papers, and ultimately getting a job!

Guide and tips for literature reading

2.1. You cannot expect to read everything.
2.2. Try to read papers that are (i) the most interesting to you and (ii) the most relevant to your and the group's research projects.
2.3. No one has time to read the entire text of every article. Read the abstract and introduction and then try to discern the major point of the paper from the Figures and Schemes. If you find something especially interesting or unclear consult the text for further details. Keep in mind when writing your own papers that these are the sections that are usually the most read.
2.4. Whenever possible, discuss with others what you have read! This will solidify your general knowledge as well as improve your understanding of what you have read.
2.5. Take particular note of papers that describe selective reactions. These are the most useful in synthetic chemistry and the most difficult to find by traditional searching techniques.

The following are journals that you should read each week and are appropriate sources for your academic learning:

Journal of the American Chemical Society
Angewandte Chemie International Edition
Chemistry – A European Journal
Chemical Communications

These journals contain useful reviews that you should keep an eye on:
Chemical Reviews
Accounts of Chemical Research
Chemical Society Reviews

Depending on your project (inorganic, organometallic, bioinorganic, etc.) you should read every issue of the following journals (they are often bi-weekly):

Inorganic Chemistry
Organometallics
Organic Letters

For these journals, the best way to keep yourself up to date is to sign up for TOC Alerts by which the publishers send you an email when a new issue is published.

You should read papers on other journals if they are relevant to your particular research. They are often found in the references of the papers you have read, or by a database search engine such as SciFinder, Web of Science, or Beilstein (Discovery Gate).

I-3. Attending seminars at EPFL

One of the best ways of keeping yourself updated with the current research is to attend research seminars. Therefore, group members are strongly recommended to attend the scientific lectures at ISIC. These include but are not limited to seminars given by outside speakers (professors, research directors, etc.), CUSO seminars, ISIC seminars, etc. It is especially important that you attend the seminars related to your research field (in a broad sense). You are encouraged to raise questions after the seminars.

I-4. Group meeting

Group meetings are held weekly (except when HU is out of town). The group meeting is a forum for the group members to discuss results and obtain new ideas. All group members are encouraged to participate in the discussions. Presentations in the group meeting are good practices for your future presentations in conferences, qualifying exams, thesis defense, and even job interviews! The group meeting is meant to be provocative, so you can be prepared to face the real world when you leave the group. You may be challenged, or may be asked to answer very simple questions that you would feel offended. Keep in mind that this is just to ensure your intellectual growth, and nothing is personal.

I-5. Publishing your work

We follow the American Chemical Society's ethic guideline for the publication of our research. See: http://pubs.acs.org/userimages/ContentEditor/1218054468605/ethics.pdf. In addition, the ACS style guide may be followed. http://pubs.acs.org/styleguide/

Authorship
From time to time, questions about authorship arise. The group follows the ACS guidelines and common practices of reputed labs.

A. Who are the authors
"The co-authors of a paper should be all those persons who have made significant scientific contributions to the work reported and who share responsibility and accountability for the results. Other contributions should be indicated in a footnote or an “Acknowledgments” section." (ACS ethical guideline)
"Generally speaking, all authors of a publication should have made significant and substantial intellectual contributions to the work being reported. ... If a colleague prepared buffers or did routine computer programming, these contributions should be acknowledged, but they are not

sufficient contributions for authorship. General discussion with colleagues or within research groups is rarely sufficient for inclusion in authorship. Despite some arbitrariness in defining what constitutes a significant intellectual contribution, the guiding ethical principle is clear and should be adhered to." (ACS style guide)
"Not everyone who contributes to a research project should necessarily be granted coauthorship on the resulting papers. Every listed author should have contributed substantially to the project with respect to its conception, the design and/or performance of the experiments, the analysis of the results, and/or the drafting of the manuscript describing the project. All authors (and especially students!) should participate in critical reading and approval of the final manuscript submitted for publication. Each author should understand the research problem and should be able to offer an intelligent discussion of the entire project from the perspective of his/her own involvement in it. There should never be any "courtesy authors," who may have been selected because of previous or future efforts in this research area or who are considered to add credibility or prestige to the publication (or to themselves), or for any other reason. Those who provide services such as statistical advice or routine analytical/administrative support should not be granted authorship but can be thanked in the acknowledgments." (Cell, 2006, 126, 823-825).

B. The order and responsibility of authors
"A question that often arises concerns the order of the authors' names. This is not really an ethical issue, and practice varies from place to place. **Most often the first author is assumed to have made the major contribution to the work, and the senior and/or corresponding author is listed last.** However, many variations to this theme exist, such as putting the authors in alphabetical order. In some cases, the specific contributions of each author are described. ... Authors should not become obsessed with this matter. Ultimately, a researcher's scientific reputation rests on the totality of publications and the significance of contributions to the field." (ACS Style guide).
"It is often said that all authors are responsible for the entire content of a manuscript. This is a meritorious ideal, but unrealistic. Most manuscripts have multiple authors, and very often, a single author is responsible for only a portion of the work being presented. A more realistic assessment of what authorship implies is that each author should have read the manuscript carefully and understood the findings, but the technical responsibility is only for the area in which a given author has the appropriate expertise. The responsibility of the corresponding author is to ensure that all authors have approved the manuscript before submission and for all subsequent revisions." (ACS Style guide).

What and when to publish
"Research should be published in a **timely** manner when enough work has been done to yield **significant** results." (ACs Style Guide) HU will discuss with the lab member(s) about publications case-by-case and make the executive decisions. A lab member is welcome to suggest and take the lead in preparing a new publication.

Writing of the paper

In general, the first-author of the paper is expected to write the main part, and coordinate the other co-authors to complete a complete version of the first draft.
Consult the papers that have been published by our group, as well as those in the literature (if they are well-written) for how you can assemble your research findings into an acceptable publication.
Note: **Plagiarism is strictly forbidden** in our group and in the whole academia! Avoid it at any cost. Never copy a whole sentence or even several phrases from other papers, books, etc. into your paper or thesis. This includes your own previous papers and the old papers of the group, as **self-plagiarism is also prohibited**. The only exception for the latter is that when you write your Ph.D. thesis, you can insert the papers of which you are the main author.

I-6. Presentation in Conferences

Due to financial and time concerns, you may attend a scientific conference only if it is related to your work and you have enough results to present, either in the poster or better in the oral form. On top of this, there is a limited budget available for travels for the whole lab. HU will make the decisions case-by-case. If justified, your meeting expense will be covered by the lab budget. If you insist on going to a meeting that does not meet the above criteria, you will have to pay for the expense on your own and the time you spend on the meeting is counted as your vacation.
Send HU a copy of your presentation (poster or oral) ideally 2 weeks, but at least 1 week before the conference. You are expected to revise it according to the feedbacks, and you may be asked to do a rehearsal for your oral talks.
Dress professionally for your presentations.

Lab Protocols II: Safety, Instrumentation, and Lab Operation

1. Laboratory safety

Safety first! Everyone working in the lab must first consult the EPFL's ***Rules of Hygiene, Safety and Environmental Protection*** (see appendix 1). 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 working in 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 in your desk, or the office area.

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. Try 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 a chemical you are working, especially if you have concerns.

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.

See section 3.1.4 and 3.1.5 of the EPFL safety booklet (pages 5-6) for rules.

All the chemicals in the gloveboxes should be inventoried according to the box number. All the other chemicals should be stored according to other internal storage methods, e.g., organic/inorganic/acid, carbon numbers, etc. Ask the person in the group who is in charge for chemical inventory if you have questions. 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. (Exemple : 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.

- This is forbidden to store alkali metals and their alloys. 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 in suitable flasks (ex. Dessociator) and, if necessary 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.

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, H_2O_2, etc) should be placed in separate waste from organic reagents/solvents. **H_2O_2 explodes when it is dried. Only use in H_2O_2 in water; never try to evaporate a reaction mixture in contact with H_2O_2.**

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.** 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. Let HU know if you need to work with azides.

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 NaN3 in chlorinated solvents.

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 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. I think Heron and Oleg have some protocols for how to handle this situation. 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.**

• 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 thioaceton!**

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. Dispose of gloves (in solid waste container beneath the hood) whenever you may have come in contact with these reagents.
III. (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, phsophines, 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 Pyrrophoric Materials

1.6.1.1 Pyrrophoric 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!**
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 uncontainable 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 can 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 uncontrolably, 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.

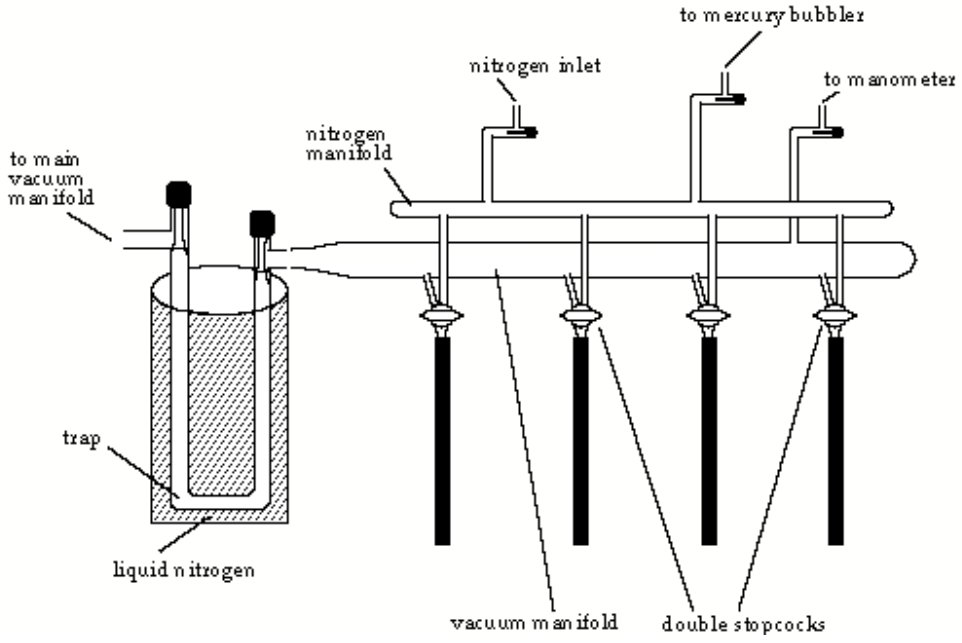
For medium or large solvent spill, use the emergency kit (mineral absorbent) which allows to collect the solvent spill on the ground. See page 11 of the EPFL safety booklet.

2. Schlenk Procedure—Using the Vacuum Line

Make sure that you never pump air in a cold trap. Oxygen will condense and explode!

The schlenk techniques are named for the Schlenk who investigated the complex structures and equilibria for common Grignard reagents in solution. These techniques have been modified and refined to deal with transition metal compounds that are sensitive to the components of normal air (dioxygen and water are typically the most problematic) and are thus also referred to as "Inert Atmosphere Techniques". Moderate-to-quite-air-sensitive compounds are routinely manipulated by these procedures in modern laboratories. Extremely air sensitive or very volatile compounds, however, are not amenable to Schlenk techniques and are handled using "**Vacuum Line Techniques**". Consult HU if you need to use these more specialized techniques.

I. Schlenk Techniques
The basic piece of equipment used in this project is the double manifold, or **Schlenk line**:



The designs of Schlenk lines vary in individual labs. For example, at EPFL, we are not allowed to use mercury bubbler, so we use a silicon oil bubbler. We use a digital vacuum manometer to monitor the vacuum, whereas in most places in the US Hg manometers are common.

Inert gas (argon or nitrogen) is provided through the top manifold. The inert gas enters from a tank via the indicated stopcock and any over pressure exits through a oil bubbler (not shown). The vacuum manifolds in Mead are all connected to one main manifold, which is isolated from the oil pump by a liquid nitrogen trap (solvents degrade pump oil). The vacuum in the individual manifolds is roughly indicated by the manometer. The main vacuum line is equipped with an electronic vacuum gauge.

There are certain hazards associated with this apparatus. First of all, any time there is pressure or vacuum in use there is a possibility of glassware failing due to fatigue. Using the oil bubbler as an outlet for the over pressure of nitrogen greatly reduces the chance of explosion, but the risk of implosion is not as readily controllable. Even glassware that is in apparently good condition can fail under vacuum as small as that provided by a water aspirator – the probabilities increase somewhat on a vacuum manifold, especially when the apparatus is subjected to thermal shocks. KEEP THE SHIELDS IN FRONT OF ANY GLASSWARE UNDER VACUUM!!
Liquid dinitrogen in an open dewar presents no hazards beyond frost bite, however, liquid dinitrogen condenses dioxygen at reduced pressure. **Should a trap cooled with liquid dinitrogen be left exposed to the air, dioxygen will condense. Liquid dioxygen is a deep blue color -- if you ever see a deep blue color in a trap, get HU immediately and follow his instructions.** If HU is not available, a general advice is to keep the vacuum on the system to pump the trap, and slowly warm up the trap (e.g., leave the trap on but not add more liquid N_2). LIQUID OXYGEN IN THE PRESENCE OF ORGANIC SOLVENTS PRESENTS AN EXTREME EXPLOSION HAZARD. We will always assume there are organic solvents in the trap.

II. PROCEDURE:

1.1 Set-up

1.1.1 Always wear safety glasses whenever working in the hood area!

1.1.2 Examine vacuum manifold to insure that it ready to be evacuated

1.1.2.1 Turn stopcocks to the horizontal position.

1.1.2.2 The liquid trap {looks like a giant glass finger} is empty and securely clamped in place.

1.1.3 Turn on vacuum pump with the switch located near the motor of the pump

1.1.3.1 Pump should become quiet within minutes indicating that there are no significant leaks

1.1.4 Connect the vacuum to the Schlenk line. This can be done by opening the corresponding stopcocks. You can notice the change in the reading of the vacuum monometer.

1.1.5 (optional) Check that the vacuum line is functioning correctly.

1.1.5.1 Test vacuum by placing thumb over one of the hoses descending from the manifold

1.1.5.2 Rotate the corresponding stopcock 90° CW such that the vacuum line is connected to your manifold.

1.1.5.3 Return stopcock to the starting position by rotating 90° CCW

1.1.6 Fill the Dewar with a small amount of Liquid N_2 (20%). Place the Dewar under vacuum trap. Adjust lab jack to appropriate height. Fill the trap with liquid N_2.

1.1.6.1 The Dewar is made of glass and is under vacuum. It will implode violently if the glass is shattered. Handle with care

1.1.6.2 Liquid N_2 is a cryogenic coolant and will cause burns to the skin if handled with bare hands

1.1.7 The vacuum line is now ready to be used.

1.2 **Shut Down**

1.2.1 Always wear safety glasses whenever working in the hood area!

1.2.2 Disconnect the pump from the manifold wither by turnoff a connection (if your vacuum line has one) or by turn off vacuum pump. **This is very important because we do not want to have the vacuum on while opening the Schlenk line to the air. To avoid condensing liquid O_2!**

1.2.3 Open one of the stopcocks to relieve the vacuum in the line by rotating 90° CW and connect the Schlenk line to air. Valve can be left in open position

1.2.4 Carefully lower the lab jack in order to remove the Dewar.

1.2.5 Remove the trap. **DO NOT add the contents of the Trap to a waste container unless it is > 0°C**

1.2.6 Vacuum trap can then be left in the hood to dry.

Note: The order of 1.2.3 and 1.2.4 can be reversed if you do them together quickly.

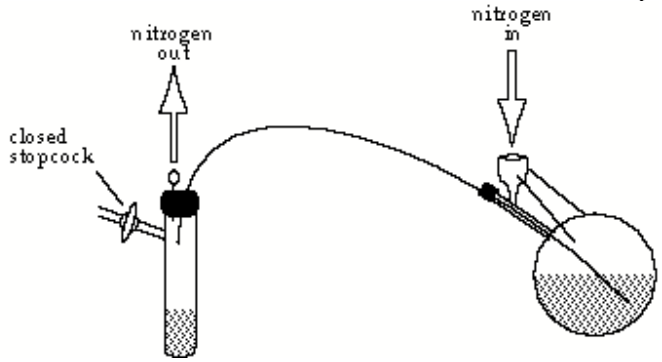
Vacuum Glassware (Schlenkware) is made with a side arm for evacuation of the apparatus and for the entering inert gas used to flush the apparatus.
Vacuum Grease should be used when assembling an apparatus for use on the double manifold. Grease should be removed using pentane, hexane, or petroleum ether, kimwipes, pipe cleaners and a pair of forceps.
A **septum** (plural "septa") is a stopper with a thin section in the middle to allow transfer of liquids in and out of the vessel with needles. Septa should always be folded down and wired when in use. *Never pump down on a septum capped flask-- always use ground glass stoppers.* Septa do not hold vacuum very well, even when they have not been pierced, and are best used only with a positive pressure of dinitrogen.

Exchanging a ground glass stopper for a septum or vice versa, requires a moderately strong flow of dinitrogen.

Pump/fill cycles are used to establish an inert atmosphere in a vessel. The vessel is sealed, but attached to the line via pressure tubing. The vessel is evacuated by opening the double stopcock so that the vacuum manifold and the hose are connected, then filled with argon by moving the stopcock until the argon manifold and the hose are connected. The argon flow should be monitored via the mercury bubbler during this procedure. For best results, pump/fill cycles should be repeated three times.

A **cannula** is a long double ended needle. It is used to transfer liquids from one vessel to another. Cannula should be kept in the oven, and purged with dinitrogen while still warm. The other end of the cannula is inserted into the receiving flask, and the stopcock closed so that the only flow of dinitrogen is through the cannula. A needle is placed in the receiving septum to vent, and the cannula is pushed into the liquid to be transferred. *Do not transfer liquids through a cannula with vacuum -- the interface of the septum and needle will leak air.*

A **cannula filter** is a long needle with a piece of filter paper tightly wired onto a lipped glass attachment at one end. These can also be made with plain cannula.



Syringes are used to transfer liquids without exposing them to air, but unlike a cannula, a flow of dinitrogen is not required. An inert atmosphere should be established in a syringe by repeatedly drawing dinitrogen into the syringe and expelling it. *Do not pull hard on a syringe to create a vacuum -- the syringe will leak.* Allow the positive pressure of the dinitrogen flow to push the barrel out. By the same token, beware that the barrel is not forced all the way out of the syringe and broken. If the compounds in question are water sensitive, the syringe should be dried in the oven and cooled in a desiccator.

3. Glove box

Glove box can be very useful if you know how to. They need careful maintenance. Always follow the rules. If you are not sure, ask!
The glove box is meant to provide the convenience for working under inert atmosphere, i.e., without O_2 and H_2O. But before it can do it, you need to make sure you do not bring even trace of O_2 and H_2O into the box. The general rule is that everything is bad for the glovebox. With a few exceptions, nothing goes into the glove boxes as it is.

Solvent scales:
I. Solvents **compatible** with the purification catalysts: Pentane, Hexane, Benzene, Toluene, Heptane, and other hydrocarbons.
II. Solvents **bad** to the catalysts: THF, Ether, DME, etc.
III. Solvents **very bad** to the catalysts: Methylene Chloride, Acetonitrile.
IV. Solvents **extremely bad** to the catalysts: Pyridine, Methanol, Chloroform, DMSO, DMF, Pyridine.
V. **Never** use as solvents: acids, water etc.

1. The box can work under three modes: circulation (blower on), purging, or neither. Under circulation, the box atmosphere goes through the catalyst for purification. The box should be under the circulation mode when not in use and when only compatible solvents are being used. Switch the circulation off when you are working with solvents/vapors that are toxic to the catalysts, e.g., solvent II to IV. After that, purge the box to regenerate the atmosphere. Normally a 30-min purge is required. If you just used small amounts of THF and ether, then a 20 min purge is enough. Do not turn back to circulation without purging.

2. Every morning, before using the box, you should purge it for 15 min.

3. Regenerate the box every 3-6 months (depending on the performance) to reactivate the catalyst. Regenerate the activated carbon.

4. Do not leave anything open in the box for too long. Solution reactions running in vials should be capped.

5. If the box atmosphere contains other vapors, purge the box for 15 min before running a routine NMR, and 30 min before making samples for a very clean NMR.

6. Be careful of solvent contamination. If you are using ether, do not open a bottle of other solvents because you don't want those solvents to contain ether as well. Purge generously if you are concerned.

7. For big antechambers, evacuate/refill for 3 times, every time 15 min. For small antechambers, evacuate/refill for 3 times, every time 5 min. Exception can be made in special circumstance (e.g. transferring crystals), but use good judgements.

8. All glasswares to be used in the box have to be heated at 150 degree for more than 3 hours before entering the antechamber. Ideally they should have been in the oven for 6 hours or more.

9. Vials to be used in the box need to be heated at 150 degree overnight before entering the antechamber. The same is for glass pipette.

10. Caps for vials need to be heated in a vacuum oven at 80 degree for 24 hours before being use in the box.

11. Kimwipes need to be heated in a vacuum oven at 120 degree for 24 hours before being used in the box.

12. Only chemicals packed under N_2 or Ar can enter the box with the caps on. For other chemicals, you always have to leave the cap off, covered the bottle with a kimwipe (can be a regular one, but you need to remove it from the box after use) and seal it with an elastic rubber band.

13. All liquids to be used in the box have to be degassed and dried. A 3-cycle freeze-pump-thaw procedure is recommended. Transfer such liquids to the box using air-free glasswares with tight seals (e.g. Teflon O-ring joint). If you are using Schlenk glasswares, you normally need to evacuate the vessel and seal the glass joints with electric tapes. This is because when pumping the antechamber, the seal can break off if the inside pressure of the vessel is not zero.

14. Reactive reagents such as Organo Li, Zn, Mg compounds normally come with a sure-seal bottle. You could take them in as it is. When you work with them, make sure the waste is treated properly because they will cause fire in the open air immediately (e.g. the second you open the antechamber). Consult me or other experienced members if you are not sure.

15. Sensitive compounds purchased from commercial sources, such as Ni(Cod)2, often come in sealed ampules, so you could take them in as it is. Make sure you seal them well in the box. Accidents happen once a while so even in the box you need to be careful how you store the compounds.

16. Label everything! Make sure the label last. For pyrolytic and explosive compounds, make sure you have multiple labels.

17. Report anything abnormal with the box. If something is not working, do not leave it.

18. Solvents from the box come from the solvent purification system. The solvents need to be tested with indicator before use. Here is the general procedure:

19. Heat glass container at 150 degree for more than 3 hours. Connect to the system, wait until it is cool, and follow the solvent purification system procedure to get the solvents. Take in the flask (which should be sealed), degas with vacuum line in the box (2 min for ether and pentane, and 5-10 min for others), then pass through a short column of activated alumina oxide. Test the solvent,

by adding a drop of indicator into 1 mL of solvent. If it passes the text, then store the rest solvent over activated molecule sieve. If it does not pass, pass through the alumina oxide again.

20. Use regular white caps for routine use; use polymer lined caps when you need good seals and when you are heating with solvents inside the vial.

21. When you use solvents III and IV, take out the corresponding trash when you finish. The same applies when you use reagents that are bad to the catalyst.

22. Thiols and Phosphines are bad for the catalyst. When working with them, make sure you turn the blower off. After the work, purge for at least 15 minutes before turning the blower on again.

23. Do not put things containing wood in the box. They often contain a lot of water that is hard to remove.

BOX RULES: extension

1. If you make a mess, clean it up. There is absolutely NO REASON for a spill to go uncleaned. This goes for a spilled reaction, or spilled alumina. If you need to clean it up with solvent and are weary of using hte tweezers to push kimwipes around (as to not dissolve the gloves), then use the green gloves that are on the top shelf on the left side of the box. If you need to clean the glass, use acetonitrile then purge the box as usual.

2. If you use solvents, replace them. When the bottles have maybe a couple cm left above the sieves, bring more in. At the very least, start collecting the solvents. When bringing them in, degas and if they fail the ketyl radical test (i drop should keep 1 mL solvent purple, or blue if its THF or ether), degas more and/or dry over alumina.

3. When vials are running low, or pippettes, put some in the oven and tell the other boxmates. We should not have to wait on vials.

4. If you use something, put it away. This goes for spatulas, bulbs, tweezers, etc. Dirty kimwipes should go in the trash. If you have a "working" kimwipe that you plan to reuse, then set it aside somewhere. And those hanging containers all have a purpose- don’t randomly throw vacuum adapters in any given one, so that the next person has to take them all down and find the right sized one.

5. Take out your trash in a timely manner.

6. Tape up all bad reagents and solvents.

7. Always keep some NMR tubes in the oven, and when we are running low on tubes, make sure to clean yours and put them in the oven.

8. Once you take out your trash, don’t let it sit in the waste hoods. Especially glasswear and frits that need to be cleaned. Stirbars can be put in the stirbar vial, which is then cleaned with acetone and aquaregia before being put back in the oven.

9. We all need to share responsibility for bringing stuff into the box. Such as NMR solvents, alumina, celite, etc. We dry stuff at about 300 degrees under vacuum for 48 hours. So when we run low, let the other people in the box know, and one of us will dry the stuff taking turns.

10. As for caps... the heater has been ordered. Green caps can be washed and reused. Otherwise white caps are heated for 48 hours under vacuum at 140 F.

11. Make sure to refill the trap during the day, ESPECIALLY if you pump off more than a vials worth of stuff.

12. When bringing stuff in/out, make sure the antichamber is closed off. If in doubt, immediately start to purge the box, and check the atmosphere. Cycle at least 5 minutes for the small, and 15 for the large. If someone just came out and you need to come out and hence the chamber is empty, you can drop the cycles down to 2' for the small and 10' for the large.

13. Purge out nasty things for 30 minutes. Also, do not open the fridges while the atmosphere is bad, and if you do, make sure to purge for 5-10 minutes with the door ajar.

14. Do not leave lab at night before talking to the other boxmates to make sure that they will take down the trap. Even if you spent all day in the office, you still need to talk to the others before you leave. The trap should never be left up by accident.

15. When bringing stuff in/out, MARK the log sheet. I don’t care if you are bringing out an IR and plan to bring the cell back in 5 minutes, because someone else in the meantime might come along and bring something out exposing our atmosphere to air.

16. If someone is using the large and you want to use the small, close off the large as you open the small to the outside and as you backfill with nitrogen. This will make things go faster with bringing stuff in, so that no extra cycles need to be added.

17. Pay attention to the nitrogen level in the big tanks. We have a problem with our solenoids. Usually the first to go is the large antichamber vacuum (check in the back to make sure the large is actually under vacuum; it should always be under dynamic vacuum not static). Next to go is the circulator. Check for error messages.

18. When two people are in the box, often the change in pressure turns off the vacuum and the circulator. Check and turn it back on.

19. Try and keep the vacuum ports clean. At the very least, the immediate area. Bumping happens and they will never all be clean, but we should be able to trust that if our stuff bumps, we did not contaminate our sample.

20. Try and notify your boxmates ahead of time if you plan to do some crazy chemistry that requires a lot of purging or nasty solvents- for example, unless i am working early in the am or late at night, I will ask you guys before I make the box benzene free for an antire afternoon.

21. If you get ANY solvent pumped up in the vacuum for the antichambers, or the trap went dry overnight and there is non-frozen solvent, the pump oil needs to immediately be changed.

22. Purge 15-20 minutes for nmr if you want a spectrum without vapor of the box (pentane, ether, for instance).

23. If heating stuff on the heat plate, tape up your vials and/or use green caps. (Especially if its benzene or toluene please!)

24. purge the box every once in a while, esp if it has not been purged all day and was been going in/out a lot. And check the atmosphere too!

25. Purge the box 15 minutes before opening the stock bottles of celite, sieves, alumina, or indicator (20 mL vial).

26. If you have any doubts or questions about whether you are doing something that is potentially harmful for the box, ask your boxmates or someone else in lab (for example what's the best way to bring in mercury?)

27. If you are using a bad solvent and walk away from the box, make sure your boxmates know. And don't open solvents or anything with the bad solvents in the atmosphere.

28. Be weary of holes in the gloves. If you find one, find your boxmates so we can take appropriate action. Also, if the box is clicking, don't walk away until the problem is solved.

4. Solvent Purification System

You must be checked out by the person in charge of this facility before using it. He/she will give you a handout with general procedures and rules for the use. He/She will show you how to use it before you are capable of doing it yourself with confidence.

5. NMR

Ask your labmates how to obtain an account and how to use the instruments. Unfortunately we do not have an organized institutional training at this moment.

6. GC, IR, UV-Vis, Rotovap

You must be checked out by the person in charge of this facility before using them. He/she will give you a handout with general procedures and rules for the use. He/She will show you how to use them before you are capable of doing them yourself with confidence.
Clean your work area after use.

7. GC-MS, MS

We use the GC-MS instrument of Prof. Jérôme Waser. Give your sample(s) to the person in the group who has access to it.
We occasionally use the institutional facility for GC-MS and MS. Notify HU before you submit samples.

8. Elemental analysis

We use the institutional facility for elemental analysis. Notify HU before you submit samples.

9. X-Ray

We use the institutional facility for X-ray Crystallographic Analysis. Notify HU before you submit samples. Make sure the facility people are aware of the potential danger of your sample (sensitivity, odor, toxicity, etc.).

10. Pumps

Pump oil should be changed two to three times a year. It is your responsibility to keep your pump clean (by avoiding contamination with solvents) and to change your pump oil on a regular basis. Remember, a clean pump will work smoother, longer, and most importantly it will pump down faster.
For problems with your pump (poor pump performance, leaking, strange noises, etc), immediately shut it down and talk to HU or contact the machine shop in order to diagnose the problem.

11. Cleaning Glassware

Note: Although it may not seem that important, cleaning glassware is one of the most important tasks that you will do in lab – contaminated glassware (along with contaminated solvents) are the two biggest causes of reactions going bad!

11.1. General Group Glassware

11.1.1. Rinse out flask into organic waste to remove organic material by washing with a H2O-miscible organic solvent like acetone, MeOH, or THF, depending on solubility.
11.1.2. Thoroughly clean grease off of all joints with hexanes and a Kimwipe.
11.1.3. Scrub both the interior and exterior of the flask vigorously with a washing brush and soap/warm water to remove salts and remaining residues.
11.1.4. Glass and Teflon stopcocks should be removed from joints before cleaning. They are easily damaged by small particles such as salts and the stopcock bore tends to hold up liquids.
11.1.5. Rinse flask with warm water (at least 2-3 times) and with distilled water (at least 2-3 times) to remove all soap/residues.
11.1.6. Finally, rinse with a small amount of acetone and place on the drying racks.
11.1.7. If glassware remains visibly dirty after this procedure **DO NOT** leave it on the drying rack for someone else to take and use!! ASK HU about the best way to get it clean – this will usually entail either placing it in the base bath and/or washing with strong acid (e.g. conc. H_2SO_4, HNO_3) to remove residual metal salts.

11.2. Frits

11.2.1. Rinse your frit with solvents in which the solids on it are soluble. Typically this would involve MeOH followed by acetone then EtOAc then CH_2Cl_2. Then, turn the frit upside-down and rinse with these solvents a second time.
11.2.2. Note that aqeous washes (i.e., those with bleach/water/acid/etc) are sometimes necessary to remove toxic reagents like Sn and/or other reagents that are soluble in these media. However, these washings need to be separated from the organic washings, and disposed of separately (see waste section). Also, washes with H_2O and/or aqueous solutions should be followed by copious rinsing with MeOH before the introduction of immiscible organics like CH_2Cl_2 or hexanes.
11.2.3 If residue remains (especially metal-based residue) it can often be removed by placing 50% conc. HCl and 50% MeOH in the frit and allowing it to drip through slowly, followed by rinses with HCl, H_2O and MeOH.
11.2.4 If any particulate matter remains on the frit and/or it is not completely white, you should place it in one of the bucket in for cleaning with piranha solution (conc. H_2SO_4/H_2O_2) or aqua regia (HCl/HNO_3). However, YOU MUST COMPLETELY REMOVE ORGANIC SOLVENTS from the frit before subjecting it to piranha solution or aqua regia (highly oxidizing!). So, rinse the frits with MeOH followed by copious water before placing them in the bucket

11.3. NMR Tubes

11.3.1. Rinse the contents of your NMR tubes into organic (or aqueous) waste (depending of the contents of the tube).
11.3.2. Rinse tubes at least one to two more times with a wash bottle into your waste before using the NMR tube cleaner. These steps are important to avoid excessive contamination of the NMR tube cleaner with everyone's samples.

11.3.3. Note that you should never stick the tip of a wash bottle into an NMR tube to wash it out. This will inevitably lead to breaking the end off the tube. Instead, always hold the bottle several cm away from the end of the tube to spray the solvent in.
11.3.4. If solids/precipitated metals remain in the tube at this point, clean it out with some solvent (typically acetone) and a pipe cleaner.
11.3.5. Use the NMR tube washer to finish cleaning the tube. Typical solvent rinses might involve MeOH followed by acetone, then EtOAc then CH_2Cl_2.
11.3.6. Note again that aqueous washings (i.e., those with bleach/water/acid/etc) are sometimes necessary to remove toxic reagents like Sn and/or when the reagents used in NMR experiments are soluble in these media. However, these washings need to be separated from the organic washings, and disposed of appropriately (see waste section). Also, washes with H_2O and/or aqueous solutions should be followed by copious rinsing with MeOH before the introduction of immiscible organics like CH_2Cl_2 or hexanes.
11.3.7. Place NMR tubes flat in the oven to dry. However do not leave them in the oven for more than ~6-8 hrs (after which they should be placed in a dessicator for storage). Leaving the NMR tubes in the oven for longer than this can lead to warping, which may cause problems with spinning, shimming and/or result in breakage in the NMR instruments.

11.4. Syringes/Needles
11.4.1. **ALL** except the disposable syringes need to be cleaned directly after use! This prevents them seizing up or clogging (often irreversibly) with dried out residues. Additionally, these expensive pieces of glassware are in limited supply and are shared between many co-workers.
11.4.2. Clean gas-tight syringes by rinsing them 2-3 times with 3-4 different solvents. Typically this would include MeOH, acetone, EtOAc, and CH_2Cl_2.
11.4.3. Gas tight syringes should be placed in the oven after cleaning without their plungers for 3-4 hrs. Longer times in the oven can lead to cracking and/or damage to the syringe. They should then be placed in a dessicator. Plungers should be wiped off and placed directly into a dessicator after cleaning. This prevents irreversible expansion/contraction of the plunger from repeated heating/cooling cycles.
11.4.4. Non-disposable needles should be rinsed thoroughly using the aspirator vacuum needle cleaner with appropriate solvents (depending on what you used, typically MeOH followed by acetone then EtOAc then CH_2Cl_2 followed again by acetone).
11.4.5. Once again, note that aqueous washing of both gas tight syringes and needles (i.e., those with bleach/water/acid/etc) are sometimes necessary to remove toxic reagents like Sn and/or when the reagents used are soluble in these media. However, these washings need to be separated from the organic washings, and disposed of appropriately (see waste section). Additionally, washes with H_2O and/or aqueous solutions should be followed by rinsing with copious MeOH before the introduction of immiscible organics like CH_2Cl_2 or hexanes.

Main References

EPFL ISIC Safety Booklet, see appendix and http://isic.epfl.ch/securite.htm
Sanford Group Manual, see: http://www.umich.edu/~mssgroup/GroupBusiness/groupbis.htm
Kubiak Lab manual, see: http://kubiak.ucsd.edu/manual/index.php
Caltech Chem5b lab manual
Group philosophy of Karsten Meyer, see: http://www.inorganic-chemistry.net/kmpages/groupphilosophy.html
Personal communications, Caroline Saouma, Seth B. Harkins.