Section 5.21 **Title:** Glovebox Use **Revision Date:** 01/17/19
Prepared By: Sungho Park and Michael Roy **P.I.:** Prof. John F. Berry

Prior Approval: This procedure is NOT considered hazardous enough that prior approval is needed from the Principal Investigator.

Involves Use of Particularly Hazardous Substance (PHS)? No
___ Carcinogen ___ Reproductive Toxin ___ High Acute Toxicity
Does this procedure require medical surveillance? No
Does this require use of a fit-tested respirator? No

Brief Description of Procedure:
Use of the gloveboxes for water- and oxygen- sensitive chemistry.

Location: *List the locations (buildings/rooms) where this procedure may be performed. For use of a PHS indicate a more precise location within the room, if appropriate, as a designated area.*
6319 ("new" double glovebox), 6325 ("old" glovebox), 6375 ("oldest" glovebox)

Chemicals Involved:
N/A

Other Hazards: *Include hazards, other than chemical, that may be present during operation of the procedure.*
No inherent hazards, but flammable solvents and/or pyrophoric materials may be used in certain situations. Consult relevant SOP(s) as needed.

Exposure Controls: *(Check all that apply)*

PPE: _X_ Safety Glasses ___ Face Shield ___Chemical Splash Goggles
___Chemical Apron ___ Gloves (Nitrile) ___ Lab Coat
___Respirator (type) _X_ Other: Long sleeves and fabric gloves

Engineering Controls:
___ Fume Hood ___Biosafety Cabinet _X_ Glove box
___ Vented gas cabinet ___Other:

Administrative Controls: *List any specific work practices needed to perform this procedure (e.g., cannot be performed alone, must notify other staff members before beginning, etc.).*

N/A

Task Hazard Control Table: *For procedures involving numerous steps, it may be convenient to indicate specific requirements for individual tasks in the table below:*

N/A

Waste Disposal: *Describe any chemical waste generated and the disposal method used.*

Dispose of material according to relevant operating procedures. Pay special attention to the disposal of pyrophoric waste originating from the glovebox.

Accidental Spills: *Describe the procedure for handling small chemical spills that may occur during this procedure. Note that for large spills it may be appropriate to call 911.*

Small spills may be cleaned with an absorbing material. After the spill has been cleaned, the material should be removed from the box and placed in a fume hood to dry or disposed of according to relevant operating procedures.

Decontamination Procedures (required for PHS use): *Describe the procedure for decontamination of personnel and equipment.*

N/A

Training: *Describe any training needed prior to performing this procedure. Include training performed in-lab and any required demonstrations of competency.*

Training is required. Training is performed by the group member(s) responsible for this apparatus or another lab member they have approved. The procedure will be demonstrated at least once and new members will be supervised their first time.

Principle Investigator Approval: I have reviewed this procedure and approved it for use. Note: Modifications to the procedure may require update to this form.

Name: John F. Berry Signature: _____ Date: _____

Introduction: The gloveboxes are here to assist you in oxygen and water sensitive chemistry. The following guidelines are given to protect the box atmosphere and longevity and ultimately your chemistry and that of the whole group. If you feel that these guidelines impede your ability to do work, talk about it with the people in charge of the glovebox and they will assist you in designing a setup that will work for you. Disregarding the guidelines compromises your chemistry as well as everyone else's. Training by one of the people in charge of the glovebox, or an individual they approve, is mandatory.

Working in the gloveboxes

- Sleeves (either from clothing or tube socks) and fabric glove liners are required to keep the outside surfaces of the black rubber gloves clean. Standard gloves and lab coats should not be worn so that the exteriors of the black rubber gloves do not become contaminated.
- When putting your arms into or removing your arms from the glovebox, do so slowly. Rapid changes in pressure can be detrimental to the glovebox, and reducing the pressure below ambient (by removing arms too quickly) may allow trace air to enter the glovebox.
- Vinyl and nitrile gloves are available in the box and are strongly encouraged, especially for new users. Not only are they helpful for reducing static, but the surface of the black gloves in the glovebox may be contaminated; therefore, it is in your best interests to use the vinyl and nitrile gloves in a lot of situations. The vinyl gloves dissolve in certain solvents, so it is helpful to use nitrile gloves when you are dealing with solvents.
- There are no trash receptacles in the glovebox. Given the limited space in a glovebox, trash should always be removed upon completion of the task. It is particularly important to remove items that were in contact with solvent.
- Make sure to turn the glovebox lights off when you are finished.

Handling solvents and liquid reagents in the gloveboxes

1. Turn off the circulator using the control box. Many solvents can damage the glovebox catalyst if the circulator is left on during use. Note: the oxygen and water sensors may not provide accurate readings while the circulator is off. Do not be alarmed by spikes in the reading while the circulator is off.
2. Amines, phosphines, and volatile titanium compounds can be particularly damaging to the catalyst; therefore, avoid using these chemicals in the glovebox when possible. Amines and phosphines bind strongly to the catalyst bed, and all of these can deposit a residue throughout the glovebox. When using these compounds, make sure the box is under a dynamic flow of N_2 (quick purge ON). After using these compounds, reseal the bottles/vials tightly with electrical tape and purge for at least an additional 30 minutes. Gloves, pipets, vials, etc. that were used to handle these compounds should also be removed immediately.
3. Do not open multiple solvent containers at the same time. Because the circulator is off, the static atmosphere dramatically increases the rate of cross-contamination between solvents. If it is necessary to use multiple solvents, dispense solvents into secondary containers and dispose of cross-contaminated excess solvent when finished. Consider the order in which solvents are used to minimize cross-contamination (e.g. open the high-boiling or non-polar solvent first), and purge the glovebox atmosphere after using each solvent. Also avoid opening the freezer if possible while solvent vapors are present.

4. When you are finished using solvents, ensure all solvent-containing vessels are well-sealed and any items that were in contact with solvent (pipets, vials, syringes, etc.) are removed from the glovebox.
5. Purge the glovebox to remove residual solvent vapor. At least 15 minutes of purging is necessary, and longer times may be required depending on the nature and quantity of the solvent used (see table below).
6. After the purge is complete, ensure the circulator is turned back on.

Solvent	Type	Minimum purge time
Benzene, toluene, alkanes	Noncoordinating	15 min.
Ether, THF, acetone	Coordinating	20 min
MeCN, chlorinated compounds, DMSO, amines	Catalyst poison	30 – 40 min.
Phosphines, volatile sulfur compounds	Catalyst poison	1 hour

Glovebox supplies

- Many communal items are stored in the glovebox. These include, but are not limited to, vials, vial caps, pipets, Kimwipes, weigh paper, syringes, and needles.
    - It is a communal responsibility to keep these items stocked. When using these items, it is everyone's responsibility to replenish these items if they are running low.
    - Replacement glassware (large vials, small vials, pipets) is kept in the oven in 6325. If you bring in replacement glassware from the oven, refill the beaker that contained the items and place it back in the oven.
- Communal solvents are also maintained in the glovebox. As with communal items, it is everyone's responsibility to refill solvents when they are running low.
    - Solvents from the stills and pentane from the SPS should be degassed and brought in using Straus flasks.
    - Other anhydrous solvents are brought in with 100 mL or 1 L sealed bottles purchased directly from vendors.
    - Most stock solvents are stored over vacuum-activated molecular sieves and should be refilled and dried over sieves overnight before general use.
        - Some solvents, such as acetone, react with sieves over time and should therefore not be stored over sieves.
- Personal supplies are often necessary to store for experiments in the glovebox. Given the limited space in a glovebox, users should keep supplies in their personal inventory bins whenever possible.
    - Avoid leaving supplies on the glovebox floor or in other communal spaces for extended periods of time.
    - Personal solvents fall under these same guidelines, with the additional note that quantities should be limited as much as possible.

Using the glovebox antechambers

- Glovebox antechambers allow materials to enter and exit the glovebox without compromising the atmosphere of the glovebox. When bringing items in, the antechamber is evacuated and then refilled with N_2 from the glovebox. Repeated cycles of evacuation and refill effectively dilute oxygen and water from the air to sub-ppm levels. Typically,

three cycles are performed. Assuming a vacuum that reduces the pressure by 99.9%, this dilutes the initial antechamber atmosphere by a factor of 10^9 (1ppb). A single cycle would only dilute the antechamber atmosphere to 0.1%.

- When possible, the smaller antechamber should be used, as it can evacuate and refill much more quickly. When both antechambers are under dynamic vacuum, oxygen and water can equilibrate between the two. Therefore, only one antechamber should be used at a time. When the antechambers are not in use, they should be left under vacuum to most effectively prevent migration of air into the glovebox. Because the large AC is used much less frequently than the small ac, the large AC can be left under static vacuum to prevent interference with the use of the small ac. You should always check the state of both antechambers and the log book before using either one.
- Note: the large antechamber doors should not be overtightened, as this can cause the door to crack and lose all functionality. When the antechamber is at full pressure, the handle should be turned one quarter turn past the onset of resistance, or just until firm. The application of vacuum then completes the seal. Do not tighten the handle when the antechamber is under vacuum, as this can place undue stress on the door when the antechamber is repressurized.

Standard intake procedure (hot glassware, dry chemicals, non-porous solids):

1. Verify that the desired antechamber is available for use.
2. Refill the antechamber to atmospheric pressure, then set it to static N_2 (all valves closed). Check that the other antechamber is not under dynamic vacuum.
3. Fill the antechamber with the materials going in
    a. Whenever possible, glassware should be dried overnight before going in. Move quickly to reduce the amount the glassware cools. The glassware should still be hot when the antechamber is closed.
    b. Dry chemicals should have Kimwipes placed between the container and cap to prevent small particles from being pulled into the vacuum. Alternatively, screw-cap containers can be left slightly loose so that gas can migrate in and out, but solid particles cannot.
4. Evacuate the antechamber until the pressure gauge indicates maximum vacuum has been achieved.
5. Refill the antechamber. Repeat the evacuation and refill process at least two additional times.
    a. Refilling a large antechamber decreases the pressure in the box enough to open the solenoid valve. Adjust the rate of antechamber refill to match the rate of glovebox refill to prevent undue wear on the solenoid. Alternatively, turn on the automatic purge function to keep the solenoid open. Do not allow the glovebox pressure to fall below ambient pressure.
6. After evacuation cycles are complete, ensure the antechamber is refilled. The valve can be left under either dynamic or static N_2 when the antechamber is being opened on the inside of the box.
7. If the antechamber will not be used again immediately, evacuate the antechamber.

Intake procedure for sealed vessels, air-sensitive solids, and liquids.

The intake procedure for these materials is largely the same as above. Note the following differences:

1. Liquids should be in sealed containers: either septum-sealed vendor bottles or Straus flasks. When possible, the Strauss flask should be sealed under reduced pressure to minimize the pressure difference between the inside of the flask and the antechamber.
2. Because the vessel going through the antechamber may leak if exposed to a full vacuum, only partial vacuum should be applied. Vacuum to 90-95% pressure reduction is often sufficient. Many more cycles are required: 9 cycles of 90% vacuum are necessary to achieve the same oxygen reduction as 3 cycles of 99.9% vacuum.

Intake procedure for porous materials (Kimwipes, cork rings, rubber products, etc.)

- The intake procedure for these materials is largely the same as for standard materials. However, the final evacuation should be left overnight. This allows trace air trapped in pores to be removed. List all items being taken in overnight in the logbook (see below).
- Hygroscopic materials should be dried under vacuum at elevated temperature, or dried according to existing procedure, before being taken into the glovebox.
    - Silica, alumina, Celite, and molecular sieves should be activated at 250 ºC under dynamic vacuum overnight.

Removal of items from the glovebox through either antechamber does not require any evacuation cycles. Ensure that the antechamber has been cycled under N_2, then open the antechamber and put in materials being removed from the glovebox. After closing the inner door, the outer door may be opened immediately and the items removed. Evacuate the antechamber if it is not going to be used again immediately.

The glovebox logbook

The glovebox logbooks are essential in facilitating the use of a glovebox by more than one person. Always promptly fill out the logbook with your initials, the date and time, and the action performed. Also check whether or not you are finished with the glovebox. The following actions require noting the logbook:

- inac (inAC): materials have been placed in the small ac or large AC and are being cycled in
- inbox/ac (AC): materials previously marked inac (inAC) have been brought into the box, leaving the ac (or AC) empty
- outbox/ac (AC): materials were removed through the ac (or AC), with the ac (or AC) being last opened to air
- inac (inAC) overnight: material is being evacuated in the ac (or AC) overnight; all items being brought in overnight must be listed, and air-sensitive compounds should be identified so others may work around them if necessary
- quickpurge or QP (duration): the box is being purged for the specified duration; the solvent or reason for purge may be specified
- vacuum: the auxiliary vacuum pump on the right-hand side of the double glove box was used; the solvent or reason for use may be specified

The logbook can also be used to indicate future use. If you require the glovebox at a specific time or plan on working after others have left and will need to use the antechambers

(thus preventing overnight evacuations from being set up), first check with other lab members to avoid time conflicts. Then, fill out the logbook for your first intended action with a clear star or asterisk to show that it is planned work.

While the logbook is critical for multiple people to use the glovebox, it is not a substitute for direct communication. When demand for the glovebox is high, always communicate directly with others to allow for everyone's needs to be met efficiently.

Other procedures

Measuring solids on the balance

1. Turn off the circulation purifier to reduce air turbulence.
2. Get rid of static in the material. You can slowly apply an anti-static gun and/or use tongs instead of hands to hold materials like glass and weigh paper.
3. After determining the mass, turn the circulation purifier back on or purge the box as necessary.

Using the auxiliary vacuum line located in the glovebox

1. Make sure the circulation purifier is turned off if using solvents.
2. Ensure a vacuum trap is attached and well-sealed, then turn on the auxiliary pump connected to the vacuum. The pump will get much quieter as it reaches a stable vacuum.
3. Place the trap into a dewar and fill the dewar with liquid nitrogen. Cover the top of the dewar with insulation to reduce condensation of water or oxygen.
4. Ensure that the knobs on the vacuum manifold in the glovebox are closed. Open the valve connecting the external vacuum line to the vacuum manifold.
5. Use the vacuum manifold as needed.
6. When finished, close the knob(s) on the vacuum manifold. Close the valve to the external vacuum line. Open a free knob on the vacuum manifold to release the static vacuum from the manifold.
7. Turn off the auxiliary pump connected to the line, remove the trap from the LN_2 dewar and then immediately release the trap portion to ambient atmosphere. Dispose of the solvent collected in the trap appropriately.
8. Purge the box according to the directions above.
9. Turn the circulation purifier back on after the purge is over.

Troubleshooting: O_2 level is high (> 1 ppm) even after a purge

Do not rely on the circulation purifier to get the O_2 level down, as this decreases the lifetime of the catalyst and increases the rate of maintenance. Purge the box for an additional 15 – 30 minutes. If the problem persists, turn the analyzer off and on in case it is malfunctioning, and purge again for an additional 15 – 30 minutes. Then turn off the purge and turn the circulation purifier back on. Wait several minutes for the analyzer to equilibrate. Repeat as necessary until the O_2 level is back to normal.

References

Portions of this SOP were inspired by or borrowed verbatim from:
http://www.chemengr.ucsb.edu/~ceweb/faculty/scott/pdf/Glovebox%20General%20Use.pdf

http://mmrc.caltech.edu/Braun/Manuals/Glovebox%20rules.pdf
http://umich.edu/~mssgroup/docs/Glovebox%20SOP_2015.pdf