Section 5.6 **Title:** Using and Maintaining the Solvent Stills

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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:

Collecting distilled solvent *via* syringe. Maintenance of solvent stills.

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.*

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Chemicals Involved:

Chemical	Physical or Health Hazard (e.g. carcinogen, corrosive)
CaH_2	Reacts violently with water: generates H_2
Mg	Flammable solid
I_2	Oxidizer
Organic solvents	Consult relevant SDSs for more details

Other Hazards: *Include hazards, other than chemical, that may be present during operation of the procedure.*

Flammable solvents, needles

Exposure Controls: *(Check all that apply)*

PPE: _X_ Safety Glasses ___ Face Shield ___Chemical Splash Goggles

___Chemical Apron _X_ Gloves (Nitrile) _X_ Lab Coat

___Respirator (type) ___Other:

Engineering Controls:

_X_ Fume Hood ___Biosafety Cabinet ___ 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.).*

Only distill / dispense one alcohol (either MeOH or EtOH) at a time. Do not distill / dispense DCM and MeCN at the same time. Notify group members of overnight refills. Do not begin refills alone.

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.*

Organic solvents - dispose of excess solvent in appropriate carboy.
Follow listed procedures for quenching CaH_2 and Mg before disposal.

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. The material should be placed in a fume hood to dry after the spill has been cleaned.

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: _____

Using and Maintaining the Solvent Stills

Still Use:

Distillation

1. Turn on the water condenser; be sure to check that water is flowing.
2. Make sure the N_2 flow is sufficient (observe a rapid flow through the bubbler; ~10 bubbles/second is sufficient).
3. Slowly drain any solvent more than one day old by turning the Teflon stopcock to release the solvent into the still pot.
4. Before distilling any solvent, check the solvent level in the still pot. If the solvent volume is near the same height as heating mantle, do not distill any solvent until the still has been refilled. Do not distill solvent to the extent that the drying agent in the still pot is brought to dryness.
5. Turn the appropriate Variac to the "ON" position. Do not adjust the power setting.
6. Allow the solvent to begin condensing on the condenser. Close the collection vessel stopcock after ~10 minutes of reflux and collect the desired amount of solvent. Turn the Variac off, but leave the water running for another 30-45 minutes until cool. Turn the N_2 down to minimal flow once cooled if not collecting solvent immediately.

Transfer

a) *Glass Syringes*
    1. Take a (matching) syringe barrel and plunger of the appropriate size hot out of the oven and allow them to cool in a desiccator.
    2. When ready, put the plunger in the barrel and take a syringe needle hot out of the oven. Secure the syringe Luer lock with pliers. (Note: Make sure the flask you intend to add solvent to has a septum on it.)
    3. Ensure the N_2 flow is sufficient, open the Teflon stopcock leading to the collection vessel on the still you are using, and insert the syringe needle through the septum. Purge the syringe by slowly filling it with N_2, then pulling the syringe out of the septum and pushing out the N_2. Repeat this purging process at least twice more for a minimum of three purges (five purges is safer).
    4. When the syringe is adequately purged, immerse the needle tip in the distilled solvent. Do not pull on the plunger. This introduces air into your solvent from leaks on the glass walls of the syringe. Gently invert the syringe such that the top of the plunger is pointed toward the floor and rotate the plunger while gravity does its job. Once solvent is in the barrel, ensure you have a good seal by rotating the plunger. You can now begin *gently* pulling on the plunger while simultaneously rotating it. Be sure not to pull too quickly to prevent introducing air into your solvent from leaks.
    5. Continue filling the syringe until you reach slightly more than your desired volume. While keeping the syringe inverted (plunger pointed at the floor), push out the N_2 headspace back into the still. Invert the syringe again such that the top of the plunger is pointed toward the ceiling and push excess solvent back into the still until the desired volume is obtained.
    6. Invert your syringe so that the plunger again is pointed towards the floor and pull a few mL of N_2 into it. Pull the needle out of the still and close the Teflon stopcock. During transport of the filled syringe, *carefully* wipe the needle tip (always wipe

away from yourself to prevent accidental stabbing with the needle) with a Kimwipe to avoid solvent evaporation that could cause H_2O to condense at the tip of the needle. Use one of your fingers to push the syringe plunger laterally against the barrel of the syringe to prevent accidental movements.

7. While keeping a slight positive pressure on the plunger (while keeping the syringe inverted so that the plunger points toward the floor) to slowly blow N_2 out of the tip of the syringe, insert the needle to the flask on your line (under N_2). Invert the syringe such that the top of the plunger points toward the ceiling and add the solvent to your flask. Note that the pressure on your line may be higher than the pressure on the stills.

b) *Plastic/Gas-Tight Syringes*

1. When ready, take a syringe needle hot out of the oven. Secure the syringe Luer lock with pliers. Allow needle to cool before attaching it to a plastic syringe. (Note: Make sure the flask you intend to add solvent to has a septum on it.)
2. Ensure the N_2 flow is sufficient (~10 bubbles/second), open the Teflon stopcock leading to the collection vessel on the still you are using, and insert the syringe needle into the septum. Purge the syringe by slowly filling it with N_2, then pulling the syringe out of the septum and pushing out the N_2. Repeat this purging process at least twice more for a minimum of three purges (five purges is safer).
3. When adequately purged, immerse the needle tip in the distilled solvent. Invert the syringe such that the plunger points toward the floor and *gently* pull on the plunger. Be sure to not pull too quickly so as not to introduce O_2 into your solvent from leaks.
4. Continue filling the syringe until you reach slightly more than your desired volume. While keeping the syringe inverted (plunger points toward the floor), push out the N_2 headspace back into the still. Invert the syringe again such that the plunger points toward the ceiling and push excess solvent back into the still until the desired volume is obtained.
5. Invert your syringe (plunger points towards the floor) and pull a few mL of N_2 into it. Pull the needle out of the still and close the Teflon stopcock. During transport of the filled syringe, *carefully* wipe the needle tip (always wipe away from yourself to prevent accidental stabbing with the needle) with a Kimwipe to avoid solvent evaporation that could cause H_2O to condense at the tip of the needle.
6. While keeping a slight positive pressure on the plunger (while keeping the syringe inverted so that the plunger points towards the floor) to slowly blow N_2 out of the tip of the syringe, insert the needle to the flask on your line (under N_2). Invert the syringe so that the plunger points towards the ceiling and add the solvent to your flask. Note that the pressure on your line may be higher than the pressure on the stills.

c) *Dispensing Outlet*

1. Take a receiving flask (e.g. Strauss flask) from the oven and cool it under vacuum or in a desiccator.
2. Ensure that the N_2 flow is sufficient (~10 bubbles/second). Place the receiving flask below the dispensing outlet of the still. Slowly open the stopcock (arrow up)

to dispense solvent into your receiving flask. Be careful not to drip solvent onto the heating mantle or heated flask.

3. When you have collected the desired amount of solvent, close the stopcock on the still. Close your receiving flask. The solvent in the receiving flask should be degassed before use.

Still Maintenance:

Variac Settings

1. Acetonitrile: 74
2. Dichloromethane: 32.
3. Ethanol: 64.
4. Methanol: 70.

Refill

1. Pre-dry solvent for the still by adding activated 3 Å molecular sieves to the solvent at least 48 hours before adding the solvent to the stills. The solvent will slowly take on water when open, so it is best to add sieves only when you know the solvent will need to be refilled soon.
2. Turn on the water condenser; be sure to check that water is flowing.
3. Make sure the N_2 flow is sufficient (~10 bubbles/second).
4. Slowly drain any solvent by turning the Teflon stopcock to release the solvent into the still pot.
5. Remove the stopper from the still pot. With a funnel, add solvent to the still pot. Do not overfill the still.
6. Put the stopper back into the still pot and ensure a good seal against the Teflon sleeve.
7. Once sealed, use rubber bands or a Keck clip to secure the stopper to the flask.
8. Turn the appropriate Variac to the "ON" position. Do not adjust the power setting.
9. Allow to reflux overnight (keep the collection vessel open). Once finished, turn the Variac off and after 30-45 minutes, turn off the condenser and turn the N_2 down to minimal flow.

Rebuild

General procedure:

1. Pre-assemble still apparatus in fume hood (ensure the still pot was dried in the oven overnight).
2. Purge atmosphere of apparatus with N_2; keep in mind the large volume that is being purged will take ample time.

a) DCM/MeCN

3. Quickly seal off the still apparatus and the still pot with septa, move the still pot into an ice bath in a fume hood, and hook up an N_2 line to the still pot and put an outlet needle through the septum. Add CaH_2 to still pot under N_2 with positive N_2 flow. For every 1L of solvent that you dry, you need to add 15 g of CaH_2 (30 g total for 2L of solvent).
4. Make sure the solvent has been pre-dried over 3 Å molecular sieves for a few days. Add solvent to the flask SLOWLY until the solvent level is above the line defined by the boundary of the heating mantle; however, do not add too much solvent or it will boil up into the still during reflux. Observe to ensure no exothermic reactions are taking place.

5. Once all of the solvent has been added, reassemble the still apparatus under positive N_2 flow, and then reflux for 16 hours to ensure dryness.

b) MeOH/EtOH

3. Quickly seal off the still apparatus and the still pot with septa, move the still pot into an ice bath in a fume hood, and hook up an N2 line to the still pot and put an outlet needle through the septum. Start by filling the still pot about halfway full of alcohol (make sure alcohol has been pre-dried over 3 Å molecular sieves for a few days). Slowly add Mg turnings to the solvent. For every 1L of solvent that you dry, you need to add 15 g of Mg. (30 g total for 2L of solvent)
4. Remove the still pot from the ice bath and add 5-10 crystals of I_2 and allow to stir for 5-6 hours under N_2 at room temperature.
5. After the brown color disappears, place the still pot back into the ice bath and SLOWLY add additional alcohol to the still pot until the solvent level is above the line defined by the boundary of the heating mantle; however, do not add too much solvent or it will boil up into the still during reflux. Observe to ensure no exothermic reactions are taking place.
6. Once all of the solvent has been added, reassemble the still apparatus under positive N_2 flow, and then reflux for 16 hours to ensure dryness.

Quenching Drying Agents from Previous Still Builds

a) Before quenching any drying agents, be sure to remove all but a small volume of solvent from the still pot via distillation.

b) CaH_2

1. It is advisable to keep a fire extinguisher nearby for this procedure.
2. Under positive N_2 flow, detach the still pot from the condenser, add an appropriately sized stir bar to the flask, and quickly attach a septum to the flask. In a separate fume hood, attach the flask to an N_2 inlet under positive flow, keeping the flask under N_2. Place the flask in an ice bath and ensure that it is stirring rapidly.
3. Under positive flow of N_2, fill the flask until it's about halfway full with toluene. Attach an outlet needle to establish a dynamic N_2 flow. Allow for the N_2 to flow for 10 minutes to ensure the headspace is clear from any residual air.
4. With a syringe, slowly add *i*PrOH dropwise to the still pot with stirring. Watch for gas bubbling; if gas bubbling is happening, stop addition of *i*PrOH until bubbling ceases. Continue addition of *i*PrOH until no more bubbling is observed.
5. With a syringe, slowly add MeOH dropwise to the still pot with stirring. Watch for gas bubbling; if gas bubbling is happening, stop addition of MeOH until and switch back to adding *i*PrOH, and again wait for cessation of gas bubbling before switching to MeOH. Continue addition of MeOH until no more bubbling is observed. Allow for the solution to stir for 10-15 minutes to ensure no more gas evolution occurs.
6. Finally, with a syringe, slowly add H_2O dropwise to the still pot with stirring. Watch for gas bubbling; if gas bubbling is happening, switch back to adding MeOH, and again wait for cessation of gas bubbling before switching to H_2O. Continue addition of H_2O until no more bubbling is observed.
7. Dilute the resulting solution with H_2O, neutralize the now basic solution to a pH between 5 and 9, and dispose of solvents in an appropriate organic solvent carboy (or

if the volume of water & alcohol is much greater than that of the organic solvents, it may be disposed of down the drain with more dilution).

b) $Mg(OR)_2$ (from Mg activated with I_2)
   1. Under positive N_2 flow, detach the still pot from the condenser, add an appropriately sized stir bar to the flask, and quickly attach a septum to the flask. In a separate fume hood, attach the flask to an N_2 inlet under positive flow, keeping the flask under N_2. Place the flask in an ice bath and ensure that it is stirring rapidly.
   2. Attach an outlet needle to establish a dynamic N_2 flow. Allow for the N_2 to flow for 10 minutes to ensure the headspace is clear from any residual air.
   3. With a syringe, slowly add H_2O dropwise to the flask with stirring. Watch for gas bubbling; if gas bubbling is happening, stop addition of H_2O until bubbling ceases. Continue addition of H_2O until no more bubbling is observed.
   4. With a syringe, slowly add 6 M HCl dropwise to the flask with stirring.
   5. Once all the white solids have dissolved from the addition of HCl, the solvents can be disposed of by slowly pouring them down the drain while flushing with copious amounts of H_2O.