Standard Operating Procedure

Task: Degassing
Date: 5/31/2014
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Background:
There are three methods for degassing solvents. Each method can sufficiently remove oxygen from a solution, but in many situations one particular method will be preferred. The primary purpose of degassing solvent is to remove oxygen, although some methods efficiently remove *all* gasses from the solution.

Degassing Methods:

- Sparge. Replace all dissolved gasses with an inert gas (nitrogen or argon).
- Boil-degas. Remove all dissolved gasses under reduced pressure.
- Freeze-Pump-Thaw. Remove all dissolved gasses under reduced pressure.

Training Requirements:

- General laboratory safety training
- Glovebox training with appropriate box czar (for pumping samples into glovebox).
- Vacuum line training by a graduate student or PI
- Freeze-pump-thaw training (for samples requiring this method).

Potential Hazards:

- Puncture with needle (for degassing vessels with needles).
- Explosion from liquid O_2 in closed system (for freeze-pump-thaw degassing method).
- Implosion from breaking glassware (such as a bomb) under vacuum (for freeze-pump-thaw degassing method).
- Broken glassware due to solvent expansion (freeze-pump-thaw method)

Special PPE Requirements:

- Blast shield nearby in case of liquid oxygen.

Materials Needed:

- Solvent for degassing.
- Vessel (scintillation vial, Schlenk flask, bomb, etc.) for solvent check for any cracks or deformities.
- Adapter to Schlenk line (for Schlenk flasks and bombs).
- Degassing tubing/needles (if needed).

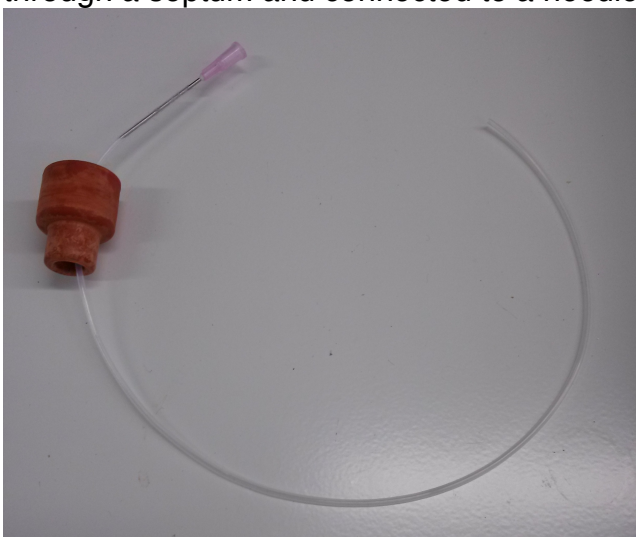
Procedure:

- *Sparge*
  - *This method is useful for high boiling solvents (e.g. water, dimethylsulfoxide), large volumes of solvents, or solvents that expand upon freezing (which can break the flask when freeze-pump-thawing). Note that significant amounts of volatile solvents can be lost to evaporation using this method.*
  - *Scintillation vial or screw-cap or septum-cap NMR tube*

- Place desired solvent/solution in scintillation vial
- Replace cap with septum
- Insert short outgassing needle (e.g. disposable syringe needle)
- Affix a long steel syringe needle to a N_2 line with a tubing-to-Luer-lock adapter
- Start a gentle N_2 flow and slowly insert the degassing needle into the solution. The needle should reach close to the bottom of the vial. Turn the N_2 flow up until a steady stream of bubbles is flowing from the end of the degassing needle
- Degas the sample for at least **20 minutes**
- After at least **20 minutes**, remove outgassing needle, then remove degassing needle.
- Use the degassed sample as needed

- *Schlenk flask*
  - Place desired solvent/solution in appropriate-sized flask (ensure correct stopcock is present)
  - Connect the (closed) side arm of the Schlenk flask to a port on a Schlenk line
  - Evacuate up to the closed stopcock, then backfill with N_2. Repeat two more times to place the tubing leading to the Schlenk flask under N_2
  - Place septum over ground glass joint
  - Insert short outgassing needle (e.g. disposable syringe needle)
  - Affix a long steel syringe needle to a N_2 line with a tubing-to-Luer-lock adapter
  - Start a gentle N_2 flow and slowly insert the degassing needle into the solution. The needle should reach close to the bottom of the flask. Turn the N_2 flow up until a steady stream of bubbles is flowing from the end of the degassing needle
  - Degas the sample for at least **20 minutes**. Remember to keep the flask stopcock closed, so that the only N_2 inlet is from the needle.
  - After at least **20 minutes**, remove the outgassing needle.
  - Open the stopcock on the side arm to allow N_2 in the flask
  - Remove the degassing needle
  - Use the degassed sample as needed
- *Teflon-sealed pressure flask ("bomb")*
  - Place desired solvent/solution in appropriate-sized flask (ensure correct Kontes valve is present)
  - Connect the side arm of the flask to a port on a Schlenk line with an adapter
  - Evacuate up to the closed stopcock, then backfill with N_2. Repeat two more times to place the tubing leading to the Schlenk flask under N_2
  - Remove Teflon valve and place a septum over the threaded opening of the flask. Note that Teflon-sealed pressure flasks typically require intermediate septum sizes (not 14/20 or 24/40).
  - Insert short outgassing needle (e.g. disposable syringe needle)
  - Affix a long steel syringe needle to a N_2 line with a tubing-to-Luer-lock adapter. For larger flasks, even long metal needles may not reach the

bottom of the solvent; instead, use a section of PTFE tubing threaded through a septum and connected to a needle (**see photo below**)



- Start a gentle N_2 flow and slowly insert the degassing needle into the solution. The tip of the needle should be close to the bottom of the flask. Turn the N_2 flow up until a steady stream of bubbles is flowing from the end of the degassing needle
- Degas the sample for at least **20 minutes**
- After at least **20 minutes**, remove the outgassing needle
- Open the Schlenk line to the side arm of the flask to allow a counterflow of N_2 in the flask
- Remove degassing needle or PTFE tubing
- Quickly remove septum (and PTFE tubing, if used) from flask while replacing with the Kontes valve **immediately**.
- Use the degassed sample as needed

- *Boil-degas*
  - *This method is one of the fastest methods, but is prone to not fully degassing the solution. Significant amounts of solvent can be lost to evaporation using this method; it is very effective for high-boiling solutions, and cooling low-boiling solutions can help minimize solvent loss. It is the only method described here that can be utilized inside a glovebox.*
  - Schlenk flask or Teflon-sealed pressure flask (“bomb”)
    - Place desired solvent/solution in appropriate-sized flask (ensure correct valves/stoppers are present). Add magnetic stir bar, if desired (see below).
    - For Schlenk flasks, seal with septum or glass stopper. For pressure flasks, seal with the Teflon stopper.
    - Connect the side arm of the Schlenk flask or bomb to a port on a Schlenk line with the appropriate adapter
    - Evacuate up to the closed stopcock, then backfill with N_2. Repeat two more times to place the tubing leading to the Schlenk flask under N_2
    - Make sure that the traps on your vacuum line are up and filled with liquid nitrogen
    - If minimizing solvent loss from a low-boiling (b.p. < 120 °C) solvent is a priority, refer to the melting point of the liquid and cool the Schlenk flask

with an appropriate water ice, dry ice, or a recirculating chiller. Do not freeze the solution! Be sure that the solution remains a suitable viscosity for gas release.

- Slowly open the stopcock to expose the solution to vacuum for 30 seconds; the solution should bubble. For best results, use a magnetic stir bar to agitate the solution and avoid "bumping" of solvent.
- Backfill with N_2, and repeat at least three times.

- Vessel inside glovebox
  - *Note: all solvents should be degassed before entering the glovebox! If you suspect a solution is not properly degassed, use this method to further degas it inside the glovebox*
  - Set up the box trap
  - Fill a vial, solvent bottle, or other flask with solvent
  - Affix the vacuum adapter to the flask
  - Slowly open the stopcock to expose the solution to vacuum for 30 seconds; the solution should bubble.
  - Backfill with N_2, and repeat at least three times.

- *Freeze-pump-thaw (FPT)*
  - *This method is best suited for precious solutions, as no solvent will be lost to evaporation. Most liquid reagents and deuterated solvents (except D_2O) should be degassed by the FPT method. Caution: solvents expand when frozen or thawed, so special care should be taken to avoid broken flasks!*
  - *Teflon-sealed pressure flask or J-Young-style NMR tube*
    - Set up the Schlenk line and traps following standard procedures
    - Fill the flask with solvent and close the Teflon valve. **Do not fill any flask beyond half-full.** Note: for deuterated solvents or situations where water is to be excluded, make sure to oven dry your glassware and evacuate while cooling before filling with solvent.
    - Securely clamp your flask such that a cooling bath can later be moved into place using a lab jack.
    - Connect the side arm of the flask to a vacuum port on a Schlenk line with an adapter
    - Open the vacuum port to evacuate the line up to the valve leading to the flask. Check the gauge on the vacuum line: ensure that the line is pumping down properly (gauge should read <50 mtorr)
    - Consider the solvent to determine the best freezing method:
      - Based on the melting point of the solvent, use a dry ice/acetone bath (melting points above –78 °C) or liquid N_2 (melting points above –196 °C). **Always use dry ice/acetone when possible!**
    - Make sure the stopcock is closed (flask under 1 atm air, tubing and line under dynamic vacuum).
    - **Freeze**: slowly immerse flask in cold bath (dry ice/ acetone or liquid N_2). You can raise the cold bath using a lab jack, or slowly submerge the flask by sliding the flask down the ring stand. Wait until solvent is completely frozen. **CAUTION: The flask is a closed system at this point, so if liquid N_2 is used to cool the flask, any leak could lead to the formation of liquid O_2.** Always continue with the procedure once you

have started a freeze-pump-thaw cycle to avoid leaving a liquid N_2-cooled flask under static vacuum. If the solvent is not freezing as expected, or if evidence of any liquid condensing in the flask is apparent, slowly open the flask to vacuum, alert researchers in the area, and set up a blast shield.

- **Pump**: once the solvent is frozen, slowly open the Kontes valve while observing the line gauge. Upon opening the valve, the gauge should "deflect" and the pressure should momentarily increase. Once the gauge is back to the minimum reading obtained before starting the procedure, close the Kontes valve.
- **Thaw**: once the valve has been closed to put the flask under static vacuum, remove the flask from the cold bath. Thaw by (a) placing the flask into a room temperature acetone bath; (b) squirting the flask with acetone (catch the drippings in a dish); or (c) using a heat gun. **Do not let flasks thaw in air**!
- Repeat this freeze-pump-thaw cycle two more times, or until the vacuum does not deflect during the pump cycle.
- After final thawing, the sample will be under static vacuum
- Use the degassed sample as needed

- Schlenk flask
  - The same general procedure can be applied.
  - The ground glass joint should be closed with a glass stopper (do not use septa, as these are prone to leak).
  - The ground glass stopcock will be used to administer vacuum, just as the Kontes valve was used above.
  - **Remember that Schlenk flasks containing liquids cannot be pumped into the glovebox!** The degassed liquid in the Schlenk flask can have a substantial vapor pressure at room temperature and should only be used for Schlenk line operations.

Additional Information and Related SOPs:

- Liquid oxygen SOP
- Bringing things into the glovebox SOP
- For additional information on cooling baths:
  - http://chemwiki.ucdavis.edu/Reference/Lab_Techniques/Cooling_baths
- For additional information on solvent melting points:
  - http://www.chem.ucla.edu/~bacher/General/30BL/tips/solvent.html