Since a large volume of the research done in the Dunbar group demands air- and water-free conditions, it becomes imperative that the solvent stills are maintained to the highest degree of standards. In a sense, they are the focal point of our research. Careful treatment of the solvent stills can be the difference between excellent results or no results at all.

The solvent stills also constitute a potential hazard in the laboratory. Careless technique, especially with alkali metal stills, can easily result in explosions. As such, it is necessary that as few people as possible are placed in charge of solvent still maintenance. Since you are reading this, it is presumed that solvent still maintenance is now YOUR responsibility.

In this treatise, I will outline the various type of solvent stills in the lab, their preparation, their continual maintenance, and their eventual decomposition. Each step in the process requires careful attention, as even the slightest mistake in certain instances can be fatal, not only to the still, but to researchers.

A. Alkali metal stills (pentane, hexanes, benzene, toluene, diethyl ether, tetrahydrofuran)

Alkali metal stills constitute potentially the greatest hazard in the laboratory, considering the tendency for alkali metals to react profusely with both oxygen and water. This reactivity, however, makes alkali metal suspensions or amalgams one of the best drying agents known, which is evidenced by their widespread use. The addition of benzophenone ([C₆H₅]₂CO) provides an easy check as to the status of the solvent still. (NOTE: Benzophenone is not used in toluene stills, since it tends to react with the solvent.)

1. Preparation

As with all other types of solvent stills, the first step is to flame-dry the 2L round-bottomed flask under vacuum (place a gas inlet adaptor into one of the 24/40 female ground-glass joints, using Teflon sleeves on the ground-glass joint itself) or to use Glassclad on the flask (dip clean flask in Glassclad, rinse Glassclad off with distilled water, rinse flask with acetone, and place in oven to dry for 5-10 minutes). Do NOT use vacuum grease on the ground-glass joints, as vacuum grease is soluble in most organic solvents. Once the flask has cooled to room temperature, refill the round-bottomed flask with an inert gas (Ar or N₂) and then evacuate and refill the flask three more times to insure that the all traces of oxygen and water are removed (this procedure should be done on a Schlenk line equipped with a MnO/silica drying column).

The drying agent (Na metal suspended in odorless mineral spirits [Aldrich]) is stored in a glove bag. The glove bag must be flushed three times to remove traces of oxygen. The 2L round-bottomed flask is taken into the glove bag, along with a small glass funnel. The drying agent is then poured into the round-
bottomed flask via the funnel (approximately 50mL of the suspension, which should appear gray with some faint purplish tinges). [Note: With a one-neck round bottomed flask, it is necessary to remove the gas inlet adaptor to add the drying agent. When the flask is removed from the glove bag, the stopcock of the gas inlet adaptor MUST be closed.] A small beaker of toluene should be available outside the glove bag, such that the glass funnel can be immersed. Any drying agent on the funnel can be decomposed by addition of small amounts of ethanol (this should be done in a fume hood).

Once the round-bottomed flask is removed from the glove bag, it is placed in the heating mantle of the still (presumably, the old round-bottomed flask has been removed). If the round-bottomed flask has more than one neck, QUICKLY remove the gas inlet adaptor (which should be on the middle neck) and replace it with the distilling head (which should have a nitrogen flow from the "house" nitrogen line). The pre-dried solvent (or anhydrous solvent, in the case of diethyl ether) can then be added via another neck. If using a one-neck round-bottomed flask, it may be necessary to remove the adaptor QUICKLY and add a layer of solvent to cover the drying agent (if the distilling head has a "sidearm", simply use the procedure for a multi-necked flask). Add at least 1.5L of solvent to the still such that the flask is approx. 85-90% full. Also add approx. four "scoopulas" full of solid benzophenone to the flask and (for pentane, hexanes, and benzene) 5-10mL of tetraethylene glycol dimethyl ether (tetraglyme) to dissolve the benzophenone. Make sure all ground-glass joints are securely closed. Wrap approx. 3-4 layers of 1" Teflon tape around ALL ground-glass joints and place a green Keck clamp on ALL ground-glass joints. The solvent should then be heated to the "collecting" temperature until the solution color is purple (this will vary for each solvent, from approx. 1-2 hours for tetrahydrofuran up to 24 hours for pentane and hexanes). Once the solution is purple, turn the heat down to the "normal" temperature. Place a jewelry tag around the neck of the flask, stating the date that the still was regenerated and by whom.

Alternate method: The use of Na/K amalgam had been discontinued due to the problems associated with the use of the glove bag to prepare the amalgam. However, recent difficulties with Na dispersions (mainly the cleaning of the glove bag following dispensing the dispersion once the bottle is less than one-half full) have caused us to rethink the usage of Na/K amalgam as a drying agent. In addition, the use of Na dispersion does not appear to be compatible with tetrahydrofuran, which appears to coagulate the dispersion. This decision is based on the ease of using sodium and potassium sand, which can be stored in the dry box.

To make an alkali metal sand, prepare a 2L round bottomed flask as you would for a solvent still, with a stir bar in the flask. Also have two small beakers of toluene (150 or 250mL beakers) ready. Remove a chunk of the alkali metal from the container (where it should be under mineral oil) [DO NOT USE THE SHAVINGS CONTAINER!!] and place it in the first toluene beaker. It will probably be necessary to cut the metal into smaller chunks that can fit easily into the round bottomed flask. If there is a large amount of oxide coating on the metal, you may want to "shave" as much of the oxide off as possible. Once the pieces are small enough to fit in the flask, place them in the second toluene beaker to make sure
that all of the mineral oil has been removed. QUICKLY add the pieces to the round bottomed flask and then evacuate the flask and refill three times. (A large quantity should be done at once, so that the procedure does not have to be repeated frequently.)

Add approximately 500mL tetrahydrofuran to the flask. Under nitrogen or argon, heat the flask with a heat gun until the solid melts (63° for potassium and 96° for sodium) and forms one "ball" of liquid in the bottom of the flask. Turn the heat gun off and allow the flask to cool slightly (but not cool enough so that the solid reforms). As the flask cools, quickly use the stir bar to stir the solution. As you do so, the alkali metal should form small spheres in the solution (you should get a wide variety of sizes). Stop stirring and allow the flask to cool to room temperature, at which time the metal should resolidify and form small solid balls of metal. Decant most of the tetrahydrofuran away and dry the solid under vacuum. The flask can then be taken into the box and the sand stored in a bottle.

To prepare the Na/K amalgam, flame-dry a 2L round bottomed flask, refill with an inert gas, and take the flask into the box (the stopcock must be open to equalize pressure). Weigh out 3g sodium sand and 9g potassium sand and add those to the flask. Remove the flask from the dry box and add 300mL toluene (enough to cover the solid). Under an inert gas atmosphere, heat the flask with a heat gun. Try to heat the potassium first; it will melt first and in turn melt the sodium. When finished, you should have a "ball" of amalgam in the bottom of the flask [alternately, one can simply heat the flask under vacuum with no toluene]. Allow the flask to cool to room temperature and then decant as much of the toluene from the flask as possible (unless, of course, the still you are making is the toluene still). Add approx. 1.5L of solvent to the flask and attach to the distilling head after adding benzophenone.

2. Maintenance

Solvent stills should be refilled when they are less than one-half full. The usual procedure is to turn the heat off and cool the flask to near room temperature before adding additional solvent (it will be necessary to increase the nitrogen flow while the flask is cooling). Once the flask is refilled, the still is heated to the "collecting" temperature (as above) to return to the purple stage. A sign should be placed on the still indicating when the still was refilled, so that others will know when the still will be ready.

Under normal circumstances, still maintenance requires little time. Under periods of heavy use (especially summer), more things can go wrong. It may become necessary to remind other group members as to SOP on solvent stills. The guidelines are as follows:

a) If someone needs a particular solvent, they should raise the heating to the "collect" setting, close the stopcock which allows the solvent to drain into the still pot, and place their name tag where it is clearly visible on the still.

b) Once enough solvent has been collected, the heat should be reduced to "normal".

c) The syringe needle used to withdraw solvent should be purged first with an inert gas before any solvent is withdrawn.
d) A small amount (not an entire syringe full) of solvent should be withdrawn to "rinse" the syringe and remove any solvent which is in between the septum and the outlet stopcock.

e) After the required amount of solvent is withdrawn, the outlet stopcock MUST BE closed to prevent leakage of air into the still.

f) If the solvent collected in the distilling head is no longer needed, the drainage stopcock should be opened (with higher nitrogen pressure) and the name tag should be removed.

At the end of the day ALL solvents should be "dropped", such that there is no solvent in the collection chamber. To remind those who may have left solvent in the chamber, you may place their name tag on their desk.

Approximately once a week, the water flow on the condensors should be checked. Since the condensers are in series (as many as eight in a row), the water flow should be quite high. You may also notice over time that the condensers will begin to pick up an orangish-brown film, which is simply rust from the water. Semi-annually, the condensors should be disconnected and cleaned with a 6M HCl solution, which converts the rust to FeCl₃. In addition, the water hoses should be changed or cleaned (depending on their condition) at this time.

During the summer, the amount of condensation on the condensors will increase dramatically. To alleviate this, simply wrap the condensors with paper towels.

3. Decomposition

Over time, as the drying agent is consumed, the color of the still will begin to change. The optimum color for an alkali metal still is dark purple. As the oxygen level increases, the color will change to blue, then to green, and eventually will reach brown. At this time, the still should be regenerated. Still decomposition will vary from solvent to solvent, so you will have to know the signs for each solvent (see Special Notes).

In preparing the decomposition of an alkali metal still, first allow the volume of solution in the still to be reduced to approx. 500mL or less (this will become relevant). Shut off the heat and allow the still to cool to room temperature. If the still is a Na/K amalgam still, drain off as much of the solution as possible without pouring out the amalgam. This is impossible with the Na dispersion stills, since the drying agent is evenly spread throughout the solution (thus the smaller amount of solvent). Add enough toluene to the still to cover the drying agent (at least 200mL). Take the flask into the hood, place a stir bar in the flask, and stir the solution behind a blast shield in the hood.

SLOWLY add a few pipets of isopropanol to the stirring flask. Once bubbles are observed, stop adding the isopropanol and allow the solution to stir until the bubbles cease (the bubbles are H₂ gas). Continue this procedure until the addition of isopropanol has no effect (this will take anywhere from one hour to overnight, depending on the amount of alkali metal present).
Next, slowly add a few pipets of distilled water to the flask. This may have little effect, if any. If bubbles are observed, follow the procedure described for isopropanol. Continue until the addition of water has no effect. At this point, the alkali metal should be decomposed. To verify this, add a small amount of dilute acid, which should destroy any remaining alkali metal. The contents of the flask can then be discarded into the waste container and the flask placed in the base bath for cleaning.

Following this procedure should cause you no problems. However, should a fire ensue from the addition of one of the reagents too quickly, do not panic. Simply close the sash of the hood and retrieve one of the ABC (or the D) fire extinguishers from the hallway (do NOT use the CO₂ extinguisher). The fire may reoccur a few times even after extinguished, so don't walk away from it until you know the system is stable (or as stable as it's ever going to get). Fires occur more frequently for potassium as opposed to sodium.

4. Special Notes

a) Pentane- The solvent should be dried over 4Å molecular sieves. Due to its low boiling point, the solvent should be refrigerated before use. Technical grade pentane is used in the stills, since it is MUCH, MUCH cheaper than reagent grade. At best, the pentane still will probably appear to be a light purple.

b) Hexanes- The solvent should be dried over 4Å molecular sieves. The hexanes still, once refilled, usually takes quite a while to recover. At best, the hexanes still will usually appear as a dark blue. (Benzophenone is not soluble in hexanes; you must add approximately 5-10 tetraglyme to the flask.)

c) Benzene- The solvent should be dried over 4Å molecular sieves. Benzene is a known carcinogen, so should not be stored with other organic solvents.

d) Toluene- The solvent should be dried over 4Å molecular sieves. Toluene does not require benzophenone, as noted above.

e) Diethyl ether- As purchased from the stockroom, the solvent is anhydrous. Addition to the still is usually done one liter at a time, so as to avoid having open cans of ether lying around the lab. Due to the propensity of diethyl ether to form peroxides, the ether solvent still MUST never be more than one year old. (Always use fresh cans of ether when refilling the still, not ones that have been opened and are sitting around the lab.)

f) Tetrahydrofuran- The solvent should be dried over 4Å molecular sieves. As stated above for ether, tetrahydrofuran also forms peroxides, thus the solvent still MUST never be more than one year old. The tetrahydrofuran still will remain purple until almost all of the drying agent is destroyed. At the first signs of color change towards brown, the still should be regenerated.

B. Phosphorus pentoxide stills (dichloromethane)
Due to the remarkable stability of NaCl and KCl, alkali metals cannot be used to dry dichloromethane. Phosphorus pentoxide is used as a substitute.

1. Preparation
The flame-drying procedure is the same as that for alkali metal stills. Once the flask has reached room temperature and been flushed three times with an inert gas, phosphorus pentoxide can simply be added to the flask either under an inert gas purge or QUICKLY in air (which is necessary if using a one-neck flask). Once added, the flask should be evacuated and refilled (since phosphorus pentoxide does not react readily with oxygen, it is necessary to "flush" oxygen from the flask). Place the still in the heating mantle and add dichloromethane (1.5L). Because P₂O₅ does not remove oxygen, it is necessary to heat dichloromethane for a longer period of time in the still before the solvent can be used.

2. Maintenance
Similar to that for alkali metal stills.

3. Decomposition
There is no color indicator available for dichloromethane. Over time, the solvent and the drying agent may turn somewhat yellowish, which is normal. Should the solvent and drying agent appear to pick up a brownish tinge, it is probably time to regenerate the still. The still should be regenerated at least once every 18 months.

To decompose the unreacted P₂O₅, pour off a majority of the solvent and add toluene to the still (approx. 300mL). P₂O₅ will not react with longer chain alcohols, but does react with methanol.

SLOWLY add a few pipets of methanol to the stirring solution. Once bubbles are observed, stop adding the methanol and allow the solution to stir until the bubbles cease (the bubbles are H₂ gas). Continue to add methanol in small portions until further addition produces no change (it may be necessary to scrape out the P₂O₅, which may become encrusted over time).

Next, slowly add a few pipets of distilled water to the flask. This may have little effect, if any. If bubbles are observed, follow the procedure described for methanol. Continue until the addition of water has no effect. At this point, there should be no solid remaining in solution. If there is, slowly add some dilute hydrochloric acid, which should dissolve any remaining solid. Discard the contents of the flask into the waste container.

4. Special Notes
Dry dichloromethane with 4Å molecular sieves. Since the solvent is carcinogenic, it should not be stored with other organic solvents.
C. Molecular sieve stills (acetone, nitromethane, acetonitrile, propionitrile)

Acetone reacts with most common drying agents, so it is necessary to distill it from molecular sieves. This method does not provide extremely dry acetone. To do this, one needs to form an acetone-Nal complex, cool the solution to allow for crystallization and then distill off the acetone.

Nitromethane, acetonitrile, and propionitrile tend to degrade when heated for long periods in the presence of various drying agents. Therefore, molecular sieves are used as well for these solvents.

1. Preparation

Flame-dry a 2L round-bottomed flask as before. Under an inert gas, add enough 3Å (NOT 4Å) molecular sieves to take up about 1/10 of the volume. Fill the remainder of the still with pre-dried solvent. Except for acetone, each of the flasks should be covered with aluminum foil.

Because of the presence of the aluminum foil, the Variac settings for these solvents should be lower than what would be expected considering their boiling points. Propionitrile will probably need to be distilled once before it is placed in the still, as it usually comes as a yellow solution (may be due to the presence of a photoinhibitor).

Each of the solvents (especially acetonitrile) are extremely difficult to dry. As such, one should expect a longer down time between refills or preparation of the still. For those who need extremely dry acetonitrile, the solvent should be eluted from an activated alumina column before use to remove as much water as possible.

2. Maintenance

Under normal conditions, the Variac setting for acetone should be zero, to avoid any possible decomposition. Only when collecting should the Variac be turned higher. For the others, the treatment is similar to that for alkali metal stills. A close watch should be kept on the Variac settings.

3. Decomposition

There isn't any. The still should be changed at least once annually, as the sieves become saturated with water. The sieves can be recycled.

4. Special Notes

a) Acetone- Use reagent grade acetone in the stills (not from the plastic containers, which contain technical grade or worse). The solvent should be dried over 3Å molecular sieves at least two months before use.

b) Nitromethane- Usually purchased in Sure-Seal bottles from Aldrich and used as received without pre-drying.

c) Acetonitrile- The solvent should be dried over 3Å molecular sieves (not 4Å).
d) Propionitrile- Usually comes as an orangish solution (Lancaster is usually the cheapest). It is necessary to pre-distill to remove the photoinhibitor before adding to the still.

D. Alkoxide stills (methanol, ethanol)

Solvent stills for methanol and ethanol are the only ones where the solvent is used to prepare the drying agent. As the drying agent is consumed, solvent is released into solution.

1. Preparation

Flame-dry a 2L flask as before with a stir bar in the flask. To the flame-dried flask add 5g magnesium turnings and 0.5g iodine. Assemble the solvent still and add 50mL of the desired alcohol to the flask (no, that doesn't mean beer, vodka, or whiskey). The solution color should be dark orange due to the dissolved I₂. Reflux the solution (i.e. turn the still to the collecting temperature) until the color of I₂ disappears. During this time, a fairly large amount of bubbling (H₂) should have been observed. The reaction, by the way, is:

\[ 2\text{ROH} + 2\text{Mg} + \text{I}_2 \rightarrow \text{Mg(OR)}_2 + \text{MgI}_2 + \text{H}_2 \]

Since magnesium reacts first with the alcohol, iodine is used as an indicator. At the end of the reaction, there should still be some magnesium turnings left in solution. Once the iodine color has disappeared, fill the still with the desired alcohol.

2. Maintenance

The solution in the flask should be stirred at all times. Otherwise, maintenance is similar to that for alkali metal stills.

3. Decomposition

As the still decomposes with reaction with water, the solvent is reformed by the reaction:

\[ \text{Mg(OR)}_2 + 2\text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 + 2\text{ROH} \]

Magnesium hydroxide, as we all know from freshman chemistry, is a fairly insoluble white solid, thus it is quite easy to tell when the still has decomposed (when large amounts of white solid have formed). To decompose the remaining magnesium alkoxide (if there is any) add water until any bubbling ceases (this should only occur if the flask gets too hot). Next, slowly add 6M HCl to dissolve the magnesium hydroxide. Discard the solution into the waste container.
4. Special Notes
   a) Methanol- Use only reagent grade and dry with 4Å molecular sieves.
   b) Ethanol- The stockroom sells two "types" of ethanol, 200 proof (100%) and 190 proof (95%). Although it is impossible to have 200 proof ethanol in the presence of any water (the highest possible is 195, or 97.5%), they sell it anyway. Use only the "200 proof" bottles as the 190 proof contains too much water. There is a BATF (Bureau of Alcohol, Tobacco, and Firearms) regulation that all ethanol must be signed out, which is their assurance that you aren't making another kind of still. It's rather a pain in the ass since ethanol is denatured before we use it, so you can't make alcohol fit for consumption with the stuff we get.

E. Conclusions

What you are about to undertake is probably one of the most thankless jobs in the history of the planet (world, excuse me, planet is one of those nasty PC buzzwords). You will get almost no credit when you do it right, but a load of blame if you do it wrong (similar to being in charge of the dry box). So, if any of your fellow labmates decide to treat you to dinner or something similar as a matter of thanks for the job you've done, order the most expensive meal on the menu. And, if anyone complains, assign that person to cover the stills when you go on vacation. And, just when you begin to think you have everything down pat, remember that there is nothing so fool-proof that a fool can't screw up.