

# Safe Use of Solvent Stills

- **Introduction:**
  - The following guide is intended to describe the minimum requirements for using the hot pot distillation technique.
  - Lab workers who intend to use the hot pot distillation technique must be trained and familiar with setting up the apparatus, running the distillation, taking down the apparatus at the conclusion of the distillation, and proper disposition of the waste. Supervisors must assure that lab workers are properly trained to operate a distillation apparatus. Lab workers should demonstrate their ability to operate and maintain the apparatus before beginning their procedure.
  - Hot pot distillation must be closely attended at all times. In some cases, literature procedures recommend preparing a solvent for distillation by refluxing overnight. In order to accommodate the standard operating procedure that no solvent is left refluxing at night, assemble the glassware the evening before and initiate the reflux in the morning during normal business hours. Distillation should always be performed with the scientist present in the building at all times. For more details, see Advanced Practical Inorganic and Metalorganic Chemistry by R J Errington, CRC Press, 1997 or Bretherick's Handbook of Reactive Chemical Hazards by L Bretherick, P G Urben, Elsevier, 1999.
- **Process**
  - The process is the reflux and subsequent distillation of organic solvents over drying materials, under argon or nitrogen gas. Most solvents can be obtained from the column purification system (Grubb's apparatus or "push still") so pot stills should only be used when there is no alternative. Pot stills must not become permanent fixtures. Ideally, the solvent should be distilled and the still taken down immediately after use.
- **Hazardous Chemicals**
  - **Solvents** (benzene, toluene, hexane, heptane, ethanol, ether, THF, chloroform, methylene chloride, etc.). Many of these solvents are flammable. Some are carcinogenic. All are toxic and should be handled in ways that minimize exposure to the employee.
  - **Drying agents** (sodium, benzophenone, magnesium, iodine, phosphorus pentoxide, calcium hydride etc). Many of these agents are potentially pyrophoric, hygroscopic, flammable, and may react violently with water. Byproducts of the distillation include hydrogen gas, metal hydroxides, phosphoric acid and organic wastes.
- **Personal Protective Equipment**
  - Basic laboratory Personal Protective Equipment (PPE) is a lab coat, gloves, eye protection and closed toe/closed-heel shoes. Additional PPE requirements are as follows:
  - **Eye protection:** Indirectly vented chemical splash goggles must be used. As a secondary precaution, a face shield is required when deactivating stills.

- **Hand protection:** Appropriately rated gloves are required when handling solvents and drying agents. Nitrile gloves are a good first choice for chemically resistant gloves. Check the glove manufacturer's chemical resistance chart for guidance on selecting the appropriate glove.
- **Engineering/Ventilation Controls**
  - A fume hood is required for distillation of any solvent. All of these stills are operated under an inert atmosphere of argon or nitrogen gas. The gas is supplied via Tygon/rubber tubing and contained within the distillation apparatus. A means to determine appropriate and continuous gas flow is required (i.e., a bubbler or flowmeter).
- **Handling Procedures**
  - **Drying Agent Preparation**
    - There are several choices of drying agent:
    - *Sodium/benzophenone* (useful for alkanes, toluene, benzene, tetrahydrofuran (THF) and other ethers): Reflux the solvent with 4g of sodium chunks, per liter of solvent, for 8 hours. Add 5 g of benzophenone and reflux for one day. When the solution is ready, the level of dryness is indicated by the color. Purple (best) > blue > green > yellow (terrible). For alkanes, it is difficult to get better than green.
    - *Magnesium/iodine* (useful for alcohol): Start with only 200 ml of alcohol. Add 2-3g of magnesium turnings and 1-2 crystals of iodine. Let stir for 5-6 hours under an inert atmosphere. Do not heat. Wait until the brown color disappears. Then add more alcohol and heat to reflux.
    - *Phosphorus pentoxide* (useful for methylene chloride): Treat methylene chloride with potassium permanganate (a few grams per liter). Shake it and let it sit for an hour or so under an inert atmosphere. Pour it into a round-bottom flask which contains 10-20g of P<sub>2</sub>O<sub>5</sub> per liter of the methylene chloride/potassium permanganate solution. Reflux for 6 hours.
  - **Distillation Procedure**
    - Start the inert gas flow at a slow rate (~1 bubble per second) and confirm that the tubing connection between the still and the inert gas is unimpeded. Check for bends, constrictions, or closed stopcocks - open closed stopcocks and replace tubing if it's damaged or appears in any way compromised.
    - Start the water flow at a strong flow rate. Check the flow rate now, after 10 minutes, and every hour thereafter. The cooling water flow rate should be sufficient to cool the condenser to obtain good reflux. Maintaining a cooling water temperature around room temp (25-27 C) is a good rule of thumb
    - Close the stopcock which is attached to the sidearm of the upper chamber reflux condenser. If possible, use a coolant (water) recycling system to conserve water.
    - Also close the teflon stopcock which leads to the collection port below the upper chamber. Open the teflon stopcock which allows solvent in the upper chamber to flow down to the lower chamber or still pot.

- Pick up the whole assembly by the still pot neck and stir it by moving it in a circular motion several times, without disconnecting the still pot from the condenser or introducing air. Confirm that there are no foreign objects between the heating mantle and the still pot. Secure the distillation apparatus to a frame to prevent damage, breakage or tipping.
  - Turn on the heating mantle to a setting appropriate for the solvent. Because temperature control for a heating mantle varies somewhat, it's best to start at a lower setting and observe the set-up for awhile to make sure reflux is reached. If reflux isn't reached, the temperature controller will need to be adjusted to a higher setting. Higher boiling solvents require a higher setting. If reflux is too violent and there's a risk of boil over, adjust the temperature to a lower setting.
  - Continue to check the water flow rate at least every hour.
  - After reflux has been achieved, wait an hour or until the color of the solution shows that the solvent is dry (as described above), whichever is later, and then close the Teflon stopcock which allows solvent in the upper chamber to flow down to the lower chamber or still pot. After the desired volume of solvent has accumulated in the upper chamber, turn off the heating mantle. Always make sure that there is at least 1/3 of the volume of the solvent still remaining (THF and ether stills in particular must NEVER be allowed to dry out as this can lead to a serious explosion hazard). At this point, watch for backflow of bubbler oil and if necessary, increase the rate of flow of the inert gas.
  - Remove the collected solvent by either of the following two methods:
  - Using a syringe (flushed twice with inert gas) with a long needle, pass the needle through a septum and then open the stopcock attached to the sidearm of the upper chamber, or
  - Attach a solvent storage flask with an O-ring to the collection port below the upper chamber. Open the Teflon stopcock on the solvent storage flask and evacuate it. Then close off the vacuum and open the Teflon stopcock in the collection port. When the solvent has transferred, close both Teflon stopcocks.
  - Open the Teflon stopcock which allows solvent in the upper chamber to flow down to the lower chamber or still pot.
  - After sufficient solvent has been distilled and collected, turn off the heating mantle temperature controller. Maintain the inert gas flow and cooling water until the still pot is cool to the touch.
- **Emergency Procedures**
  - Shut off the power at the circuit breakers, not at the heating mantles. The switches and wall sockets are close to the mantles and, therefore; would be in a danger zone during an emergency.
  - Evacuate the lab, closing the lab door, and call 911 (from a campus or cell phone) or pull the fire alarm.
  - The Fire Department will stabilize the emergency, leaving clean up to lab personnel. Only trained lab personnel should attempt to clean up after a still

accident. As another option, an outside contractor can be engaged to effect cleanup.

- If lab personnel choose to clean up after the accident, the following procedure needs to be followed. NOTE: Do not use water! Unreacted sodium and flammable solvent vapors are two hazards that exist following a still accident. Wear appropriate personal protective equipment, including goggles and face shield, lab coat, and heavy Viton (or similar) gloves with gauntlets over the sleeves of the lab coat. Sturdy shoes (not sneakers – leather shoes preferred) that cover the entire foot are recommended. Make sure power is off to the apparatus at the circuit breaker and that other heat- or spark- producing equipment nearby is turned off. Broken glass, contaminated with hazardous materials, must be disposed as hazardous waste. Clean up materials (vermiculite, paper towels, etc.) must also be disposed as hazardous waste. Be sure enough suitable containers are ready to receive hazardous waste *before* clean up begins.
- **Waste Disposal**
  - ***Still Quench Procedure***
    - Collect most of the solvent in the upper chamber. The still pot is flushed with argon and deactivated by the following procedures while still under argon:
    - *Sodium/benzophenone mixtures*: Add a small aliquot of *t*-butanol or isopropyl alcohol. With a metal or rubber spatula, break up all chunks. Stir the mixture thoroughly. Gas bubbles will evolve as the reaction progresses. Repeat until no further reaction (no evidence of gas evolution) occurs. Add a small aliquot of ethanol. Break up all chunks. Repeat until no further reaction (no evidence of gas evolution) occurs. Be absolutely sure there is no more sodium before treating with water. Break up all chunks. Repeat until no further reaction (no evidence of gas evolution) occurs. After making sure the pH of the aqueous (bottom) layer is neutral, dispose the aqueous layer as aqueous hazardous waste. The organic (top) layer must be disposed as organic hazardous waste.
    - *Magnesium/iodine*: Slowly add a small aliquot of dilute hydrochloric acid. Gas bubbles will evolve as the reaction progresses. Continue to add small aliquots of dilute hydrochloric acid, with thorough stirring, until there is no further reaction. After making sure the pH of the aqueous layer is neutral, dispose the aqueous (bottom) layer as aqueous hazardous waste. The organic (top) layer must be disposed as organic hazardous waste.
    - *Phosphorus pentoxide* (for this mixture, the argon atmosphere is not necessary): Add water *slowly*. Gas bubbles will evolve as the reaction progresses. After the reaction is complete (no further evolution of gas), neutralize with sodium bicarbonate. After making sure the pH of the aqueous (bottom) layer is neutral, dispose the aqueous layer as aqueous hazardous waste. The organic (top) layer must be disposed as organic hazardous waste.
    - Alternatively, the following procedure may be used to quench a still.

- Decant the bulk of the remaining solvent into the appropriate labeled container. Place the still pot into an ice-water bucket, and secure it with a clamp and ring stand, if necessary, to prevent it from falling over. Aim the mouth of the still pot away from any people or equipment. If you are quenching a large volume of alkali metal or metal hydride, obtain and use a blast shield, clamped to the fume hood work surface.
- Use a pipette to add a small aliquot of sec-butanol. If gas bubbles appear, wait until they stop, then add another small aliquot of sec-butanol. Continue this cautious stepwise addition until the generation of gas bubbles becomes very slow.
- After the sec-butanol has been added, try adding an alcohol with more freely available protons, such as n-butanol. Continue the same cautious step wise approach until the gas-bubble generation slows considerably. Remember to stir or swirl the flask occasionally, always keeping the mouth of the flask pointed away from anyone.
- Once you have used n-butanol, try the same stepwise, cautious addition with these solvents in sequence: isopropyl alcohol, ethanol, methanol, and water. Be very careful with the addition of water. Even after methanol has been added, the drying agent can still react violently with water, especially if there hasn't been sufficient mechanical stirring of the solution.
- Once the reaction with water is complete, use a suitable acid solution (such as 3 M HCl) to neutralize the basic solution you have created. Add the acid in aliquots with the goal of obtaining a neutral pH.
- Pour this solution into a properly labeled waste container and dispose as a hazardous waste. In order to properly label the waste container with the percentages, you must keep track of the approximate amounts of the various solvents you used in this quenching process.
- Remember that quenching a still pot can be a delicate business, particularly if the still has not been properly maintained. The potential for fire and explosion is high. If you have never quenched a still before, it is essential that you work with someone who is experienced in this area. Do not attempt to quench a still pot if you are alone in the lab.
- ***Reactive Metal Wastes***
  - Some lab groups have procedures for disposing small amounts of reactive metal wastes such as sodium, potassium, and sodium hydride. While the procedures may vary by lab group, the general procedure is the same as used for quenching still pots. Start by adding a mild quenching agent (t-butyl alcohol) and gradually progress to stronger agents (isopropyl alcohol, ethanol). Let the reaction mixture stand in the fume hood for several hours or better, overnight. When the reactive metal has completely reacted, check the pH and adjust as necessary. The mixture still has to be disposed as hazardous waste because it is a flammable liquid.
- **Prior Approval**

- Use of hot pot solvent stills is restricted to those researchers who have been trained in their use by the Principal Investigator (PI) or by an experienced user with the specific approval of the PI.
- Permission from the PI is required before any of the following solvents may be distilled using a hot pot apparatus: benzene, carbon tetrachloride, any other carcinogenic solvent, or any solvent with a boiling point higher than 130°C.
- Potassium or potassium/mercury amalgam may not be used in a solvent still without the specific permission of the PI.
- **Decontamination**
  - See waste disposal
- **Preventive measures**
  - **NEVER** leave the apparatus unattended. The still pot could overheat or run dry and result in an explosion.
  - Plexiglass shields, attached to the work surface with clamps or similar, are placed around the still in order to protect workers in case of a serious accident.
  - Deactivation of the stills must be performed under argon, not air, and by the special procedure described above.
  - Never add fresh solvent, drying agent or indicator while the still is hot. Do not dismantle the equipment while the still is hot.
- **Maintenance:**
  - Check that all water lines are adequately wired or clamped to the condenser and water source and are not cracked or weakened. Check whether the mantle is in reasonable condition and electrical cords are in good repair and not frayed or cracked.
  - Do not allow material to accumulate in the bottom of the still. Deactivate the still according to the procedure above, immediately after use. Solvent stills are not intended to be permanent installations.
  - If maintenance must occur on the building utilities, make sure the still is cool to the touch and turn off cooling water at the tap, turn off inert gas at the cylinder and unplug the heating mantle from the electrical outlet.