

# **Standard Operating Procedure for Distillation of Organic Solvents**

## **Introduction:**

Purification and recovery of organic solvents by distillation is a common laboratory operation. Instructions and descriptions for the distillations of hexanes, tetrahydrofuran (THF), diethyl ether, dimethoxyethane, benzene, toluene and dichloromethane are included in this SOP.

### **i) Storage of Solvents and General Information:**

#### **ii) Hazard Assessment:**

#### **iii) Setting up and Maintenance of Solvent Stills:**

#### **iv) Quenching of Expired Stills:**

### **i) Storage of Solvents and General Information:**

The storage of flammable and combustible liquids in a laboratory, shop or building area must be kept to the minimum needed for research and/or operations. Standard 4L bottles should NOT be stored outside of an approved vented storage cabinet. Ventilation is recommended for the storage of large quantities of Class 1A flammable liquids (such as Diethyl Ether or Pentane) or malodorous compounds such as mercaptans. Some flammable liquids such as Benzene, Methyl Mercaptan, and Carbon Disulfide, may require Designated Storage Areas.

## **Personal Protective and Emergency Equipment:**

### **A. Eye and Face Protection**

At a minimum, safety glasses with permanently attached top and side shields must be worn in the laboratory. These glasses, however, do NOT protect against splash hazards. When performing a hazardous activity such as adding sodium to or neutralizing sodium in the distillation pot, a face shield must be worn in addition to the safety glasses OR switch to chemical splash goggles (with shielded ventilation ports).

### **B. Gloves**

Appropriate gloves should be worn when handling organic solvents.

### **C. Protective Clothing**

Lab coats, closed toed shoes and long sleeved clothing should be worn when performing distillations. Additional protective clothing, such as aprons or full-length arm protection, should be worn if the possibility of skin contact is likely.

### **D. Fire Extinguishers**

All laboratories must contain at least one Carbon Dioxide (Type B-C) or Dry Chemical (Type A-B-C) fire extinguisher. Additional fire extinguishers are located near exits and/or stairwells in each building. Special Class D fire extinguishers are available for fires caused by reactive metals such as sodium. A dry-powder fire extinguisher should be readily available when working with sodium in charging or cleaning the still pot.

### **E. General**

Ensure you know the location and proper operation of the nearest fire extinguisher, eyewash station, emergency shower and fireblanket before continuing.

### **ii) Hazard Assessment:**

A Hazard Assessment should be performed for work involving distillations of organic liquids and should thoroughly address issues relating to residual water and possible decomposition of the solvent in question as well as the physical placement of the distillation apparatus and heating equipment to be employed.

#### Equipment and Location:

All stills should be assembled inside a fume hood. The size of the still should be kept to the minimum volume necessary. Do not store solvent waste bottles or any other flammable material in such a hood. Check also the contents of the cupboard underneath the hood. Consider what might happen in the event of a fire and take the appropriate precaution. If using a heating mantle and variac controller, make sure all of the wiring is sound to avoid electrical shock hazards and ignition sources. All solvents should be distilled into a receiver containing an overflow connector to prevent accidental drying out of the distillation flask. Variacs should be placed outside of the fume-hood if possible, ideally attached to the upper wall of the fume hood. Avoid dangling wires on the outside of the fume-hood.

#### Residual water contamination:

To begin with, only freshly purchased high-grade solvents should be used. Before adding a drying agent (sodium metal, LAH,  $\text{CaH}_2$ ,  $\text{P}_2\text{O}_5$  etc), test for the presence of water by pouring a small volume (1-2mL) of the solvent into a flask and carefully adding a small portion of the drying agent in question. Ethers such as THF and DME can contain significant amounts of water and might have to be pre-dried over activated molecular sieves before filtration and drying over sodium metal.

#### Decomposition:

Some flammable liquids, such as low molecular weight ethers and vinyl compounds, THF, and Dioxane, slowly form peroxides upon exposure to air and sunlight. This may necessitate periodic testing for peroxides. A simple test can be carried out involving addition of the suspect solvent to a freshly prepared solution of KI in water. An immediate yellow colouration is indicative of the presence of peroxides. Such solvents should be disposed of in the prescribed manner rather than attempted purification.

#### Drying agents:

Your supervisor will prescribe the proper drying agent to be employed for the specific solvent in question. If in doubt, ASK! For example, attempted drying of dichloromethane over sodium will lead to the generation of explosive carbenes. Only dry a solvent over a metal such as sodium if it is absolutely necessary. In many cases, high grade solvents such as Aldrich septa-sealed THF (99.9%) may be used directly for Grignard reactions or LAH reductions. The use of potassium or sodium-potassium alloys is not recommended unless absolutely necessary.

#### Inert gases:

The use of purified argon or nitrogen is recommended. If using in-house nitrogen, this should be considered "wet" and appropriate action taken, such as purging through a drying agent.

#### Operation of Stills:

The operator who starts a still has taken upon themselves the responsibility to supervise the distillation process and properly shut down the still when completed. Make sure the still is clearly labeled with solvent and drying agent (eg THF/Na or DCM/ $\text{CaH}_2$  etc) on a note attached outside of the hood. When the still is operation, the fume-hood sash should be pulled down completely. Consider what might happen if such a still catches fire or explodes! Stills should NOT be run overnight on "simmer" mode unless this operation is specifically approved by your supervisor.

iii) **Setting up and Maintenance of Solvent Stills:**

A. Setting-Up Solvent Stills

1. Set-Up and equipment will be provided by your supervisor.
2. Charging and Using Stills
  - a. A hazard assessment should be performed as outlined above.
  - a. Ensure that the still (heating mantle) is cooled down to room temperature. Ensure the variac is turned off. Glassware should be oven-dried and carefully inspected for star-cracks or other deformations.
  - b. The solvent is poured into the round bottom flask which serves as the still pot to no more than 2/3 of its capacity. Under a flow of inert gas, add the drying agent to the solvent in small portions.
  - c. Be conscious of not starting the flow of cold water through the condenser until the apparatus is fully assembled under an inert gas flow. This is likely to cause formation of a film of condensed water (particularly in the summer months) on the *inside* of the condenser.

**Some more specific general protocols follow:**

**Hexanes, Tetrahydrofuran, Dimethyl Ether, Dimethoxyethane or Benzene.**

- i. In a fume hood, a small amount of metallic sodium is cut into small pieces. The sodium may be quickly rinsed with a minimum amount of dry hexanes to remove the oil before the sodium is added to the solvent in the distillation flask. (**Note.** Sodium metal and hexanes is a potential fire hazard. Ensure that a dry-powder fire extinguisher is near by and accessible before you begin working with sodium.)
- ii. Add 10-15 mg of benzophenone to the distillation flask, establish the inert atmosphere, and bring the solution to reflux for several hours to allow the sodium metal a chance to dry the solvent. When dry, the solution will have a deep blue to blue-green color.
- iii. If, after refluxing for several hours, the deep blue color does not develop, consult your supervisor before repeating steps i and ii.

**Toluene or Dichloromethane.**

A small amount of calcium hydride is added and the solution is refluxed under a nitrogen atmosphere to dry the solvent. Note that toluene may also be dried over sodium metal hence the necessity of clearly labeling the distillation unit as detailed above.

B. **Maintenance and Inspections:**

1. Daily:

Nitrogen or argon:

- Check tank pressure gauge and replace tank if below 100 psig.
- Check flow rate at the flow meter and adjust accordingly.
- Check for flow at the bubbler and check bubbler level.

Water:

- Check flow rate.
- Check water lines and connections for weak spots and leaks.

Still Pot:

- Check solvent level is at least 1/3 full.
- Check solvent color.

Night or Finished:

Turn off the variac.  
Drain the distillation trap.  
When cool, turn off condenser.

2. Monthly:
  - Check nitrogen lines.
  - Change rubber septa on distillation trap.
3. Quarterly:
  - Check electrical wiring and variacs.
  - Check glassware integrity.
4. Cleaning:
  - Do as needed.

iv) **Quenching of Expired Stills:**

Your supervisor will instruct you of the specific protocol to be followed. Some general guidelines follow.

**Quenching sodium (from Hexanes, Tetrahydrofuran, Diethyl Ether, Dimethoxyethane, Toluene or Benzene):**

- i. After the solvent has cooled to room temperature, all potential sources of ignition and potentially flammable materials are removed from the fume hood.
- ii. The residual solvent is carefully quenched with small amounts of 2-propanol added under a blanket of nitrogen over several hours and allowed to stand overnight.
- iii. The residual solvent is then carefully quenched with small amounts of absolute methanol until all the sodium metal is destroyed. Be wary that large pieces of sodium may take several *days* to fully react. Now carefully add water dropwise under nitrogen and properly dispose of the contents.

**Quenching calcium hydride (from Toluene or Dichloromethane):**

- i. After the solvent has cooled to room temperature, all potential sources of ignition and potentially flammable materials are removed from the fume hood.
- ii. The residual solvent is then carefully quenched with small amounts of absolute methanol added under a blanket of nitrogen over several hours and allowed to stand overnight.
- iii. The residual solvent is then carefully quenched with small amounts of water under nitrogen and properly disposed of.

**Quenching potassium or sodium/potassium alloy: Extreme caution needed. See your supervisor.**

**References:**

See your Laboratory Supervisor for specific training instruction and references.

1. *Vogel's Textbook of Practical Organic Chemistry*, 5<sup>th</sup> Ed.; B.S. Furnis, et.al. Eds.; Longman: Singapore, 1989.
2. *Purification of Laboratory Chemicals*, 2<sup>nd</sup> Ed.; D.D. Perrin, W.L.F. Amarego, D.R. Perrin; Pergammon: Oxford, 1980.
3. *Organic Solvents, Physical Properties and Methods of Purification*, 3<sup>rd</sup> Ed.; J.A. Riddick, W.B. Bunger; Wiley-Interscience: New York, 1970.
4. *Experimental Organic Chemistry*, L.M. Harwood, C.J. Moody, Blackwell Scientific, Oxford, 1989.
5. *The Chemist's Companion*, A.J. Gordon, R. A. Ford, Wiley, New York, 1972.