

## VI. Standard Operating Procedures (SOPs)

### *C. Drying Solvents*

Many of the reactions in our lab require the use of dry solvents. Purchasing dry solvents is expensive, so we distill the solvents needed. Responsibility for various solvents is assigned to different group members.

Solvent	b.p. (°C)	Method	Post Purification Drying	Person In-charge
DCM	40	CaH <sub>2</sub>	4A Molecular Sieves	Anna/John /Chao
TEA	90	KOH	4A Molecular Sieves	
DMF	152	CaH <sub>2</sub> /Filter and then Distill	4A Molecular Sieves	Kaushik
Chloroform	61.2	P <sub>2</sub> O <sub>5</sub>	4A Molecular Sieves	Anna
Acetone	56	Drierite/ CaSO <sub>4</sub>	NOT UNDER Mol. Sieves	Shuangyi
Toluene	111	CaH <sub>2</sub>	4A Molecular Sieves	John
THF	67	-	4A Molecular Sieves	Ying
Hexane	69	CaH <sub>2</sub>	4A Molecular Sieves	Anna
Ether	34.5	CaH <sub>2</sub>	4A Molecular Sieves	Kaushik
Dioxane	101	CaH <sub>2</sub>	4A Molecular Sieves	Chao

*Note: When the solvent is to be distilled after standing over a desiccant, the drying agent should be filtered off before distillation if it removes water reversibly, e.g by hydrate formation (MgSO<sub>4</sub>, CaCl<sub>2</sub>), or by absorption (molecular sieves). The solvent can be distilled without removal of the desiccant in cases where water removal is irreversible (CaH<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>).*

#### **Calcium hydride, CaH<sub>2</sub>**

The reagent of choice for rigorous drying amines, pyridines, and HMPA, and effective also for drying hydrocarbons, alcohols, ethers, and DMF. It is available in powdered or granular form; the granular is preferable if it is to be stored for any length of time. The granules should be crushed immediately before use and residues should be destroyed by careful addition of water.

#### **Calcium chloride, CaCl<sub>2</sub>**

Both the powder and pellet forms are effective for pre-drying hydrocarbons and ethers. It reacts with acids, alcohols, amines and some carbonyl compounds.

#### **Calcium sulfate (Drierite), CaSO<sub>4</sub>**

It is only suitable for drying organic extracts. The blue self-indicating version should not be used to dry liquids because the colored compounds may leach into the solvent.

#### **Magnesium, Mg**

Recommended for methanol and ethanol.

## Molecular sieves

After activation at 250 - 320 °C for a minimum of 3h they are probably the most powerful desiccant available. Not useful for drying acetone because they cause self-condensation.

*4A Beads* - drying of amines, DMF, DMSO, and HMPA (store over 5% w/v).

*3A Beads* - drying acetonitrile, methanol, and ethanol.

Sieves can be reused, if not discolored, by washing well with a volatile organic solvent (acetone), allowing to dry, drying at 100 °C overnight, and then reactivating at 300 °C (4 hours).

## Potassium hydroxide, KOH

Freshly powdered KOH is a good drying agent for amines and pyridines but is inferior to calcium hydride. It should not be used with base sensitive solvents.

## Distillation Procedure

1. Charge a round bottom flask with the appropriate solvent/drying agent combination, place it in a cold heating oil bath and attach the rest of the distillation setup (water-cooled condenser, distillation receiving flask) making sure that it is connected to the N<sub>2</sub> line.



### *Distillation receiving flask / dry solvent storage flask*

2. Start the N<sub>2</sub> flow at a slow rate (~1 bubble per second) and confirm that the tubing connection between the still and the N<sub>2</sub> flow is not obstructed (ie. check for bends, constrictions, or closed stopcocks and open them).
3. Start the water at a rate strong enough that flow fills the exit tube but not so strong that the flow is turbulent or excessive pressure builds up.
4. Open the teflon stopcock which allows solvent in the flask to flow down to the collection flask. Turn on the heating plate to a setting appropriate for the solvent (ie. higher boiling solvents require a higher setting, see Table). Adjust later if necessary.

5. Collect most but not all of the solvent in the flask. At least 50 mL should remain in the boiling flask. The remnants of solvent and drying agent must be deactivated by the following procedures while still under argon or N<sub>2</sub>:

- **Sodium/benzophenone mixtures:** Inject isopropyl alcohol (a few drops, then after 10 minutes a few mL) through the stopcock using a syringe while N<sub>2</sub> gas is flowing. Then break up all chunks of sodium and sodium salts using a very large spatula (you will have to flush with N<sub>2</sub> again after that). Repeat until no further reaction occurs. Treat similarly with ethanol. Break up all chunks. Repeat until no further reaction occurs. Treat similarly with water. Break up all chunks. Repeat until no further reaction occurs. Be absolutely sure there is no more sodium. Add 500 mL more water, then separate the organic and aqueous layers, if possible. The aqueous layer will contain less than 24% alcohol and therefore can be poured down the drain. The organic layer is now waste and should be put into a properly labeled organic hazardous waste container. If the layers can not be separated, then the entire mixture should be put into a properly labeled organic hazardous waste container.
- **Magnesium/iodine:** Treat with dilute (1 M) hydrochloric acid slowly, until there is no further reaction and no magnesium is visible. Neutralize the aqueous phase with sodium bicarbonate (if necessary). The aqueous phase is now nonhazardous and can be poured down the drain. The organic fraction should be put into a properly labeled organic hazardous waste container.
- **Calcium hydride:** Treat with ethanol water mixture (1:1 by volume) until the hydrogen gas evolution has stopped under ice bath. Dilute with water and pour the aqueous solution down the drain. The white stuff inside flask can be cleaned with dilute HCl.
- **Phosphorus pentoxide** (for this mixture the argon atmosphere is not necessary): Add water slowly, until there is no further reaction. After the reaction is complete, neutralize with sodium bicarbonate and then pour the aqueous portion down the drain. The organic waste should be put into a properly labeled organic hazardous waste container.