

### 3.15. Solvent Stills – Procedures for Set-up, Use, and Neutralization

Although the procedures for purifying laboratory chemicals are inherently safe, care must be exercised if hazards are to be avoided. Solvent distillation equipment in which flammable liquids are purified by distillation with reactive metals or metal hydrides, such as sodium, potassium, calcium hydride and lithium aluminum hydride, are possibly the greatest danger in any organic chemistry laboratory. The potential fire and explosion hazards associated with the combination of air- and/or water-reactive metals with large amounts of organic solvents are great and the effects on personnel and equipment can be catastrophic. The chances of personnel escaping such an incident unharmed are very low. Consider using alternative solvent purification systems and methods before proceeding (see column purification method below for a procedure that avoids all heat and distillation).

#### 3.15.1. Set-Up and Operation

1. Use proper personal protective equipment (e.g., gloves, safety glasses, and fire-resistant or all cotton lab coat) while operating a distillation unit.
2. Any solvent stills containing reactive metals should be located in a fume hood.
3. After set up and before start up get prior approval and a final equipment check from the principal investigator.
4. The total volume of solvent used in these stills shall be kept to a minimum (BUT they should never be allowed to go “dry”). Their useful working volume is  $\frac{1}{4}$  to  $\frac{2}{3}$  of filled capacity.
5. Stills should be operated under an inert gas atmosphere of nitrogen or argon.
6. Several types of drying agents can be used:
  - a) Sodium, potassium or sodium-potassium alloys must never be used for solvents containing C-Cl or O-H bonds.
  - b) Because of their pyrophoric nature (possible spontaneous ignition upon contact with air) the use of sodium/potassium alloys (NaK), which are liquids at ambient temperature should be avoided. Solvent flasks containing lithium aluminum hydride must never be heated. As a drying agent lithium aluminum hydride is therefore only suitable for non-reducible solvents that can be obtained pure by flask-to-flask vacuum-transfer at ambient temperature.
  - c) The use of potassium alone is recommended for THF only – in these solvents the metal will melt providing a fresh & reactive surface. Be aware that it is much more reactive than sodium, especially when quenching a solvent still (see below).
  - d) The use of sodium alone is recommended for diethyl ether and all other hydrocarbons such as toluene, benzene, pentane, hexane, heptane, etc.
  - e) Calcium hydride is recommended for methylene chloride and other halogenated solvents.
  - f) Magnesium/Iodine is recommended for methanol and ethanol.
  - g) For all high boiling solvents the use of 4 Å molecular sieves (activated by heating under full dynamic vacuum overnight) is recommended.
7. Solvent stills should never be left running (i.e., being heated to reflux) while unattended – especially not overnight.
8. Stills must be deactivated and restarted with all fresh solvent and drying agents on a regular basis to avoid buildup of metal hydroxides and benzophenone “cakes” that would impair stirring necessary during deactivation. Record the date of maintenance activities at the still for reference.
9. To deactivate a solvent still containing reactive metals follow the procedure below for deactivation and neutralization.

*Reference: Armarego, W.L.F., Perrin, D.D., Purification of Laboratory Chemicals, Fourth Edition, 1998.*

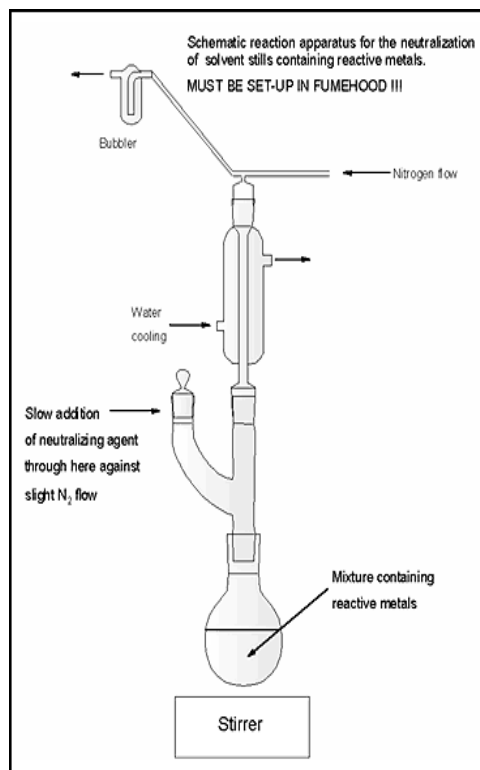
### 3.15.2. Deactivation and Neutralization

Please read and follow these procedures carefully. This procedure can be dangerous and requires plenty of time to complete. Do not rush the process. Only properly trained persons are to perform this procedure.

1. Deactivation and neutralization must be performed immediately when there is no longer a need for the distillation process. Do not abandon distillation units for others to decommission. If an abandoned unit is discovered, do not touch it and contact IUEHS for your respective campus immediately (see pgs. ix-xi).
2. Notify other laboratory occupants and your supervisor of your intent to perform this procedure. Do not perform this procedure "after-hours".
3. Wear a lab coat, safety glasses, face shield, and appropriate gloves. Familiarize yourself with the location of the nearest emergency shower, fire blanket, and exit. Have a dry-chemical fire extinguisher available.
4. Inspect the still flask. The still flask should not be more than 1/5 full and the mixture must be stirring freely using a magnetic stir bar. If it is not, carefully attempt to break up any solid deposits in the flask using a large spatula. If this does not work, seek assistance from your supervisor.
5. In a fume hood cleared of all other reactions and equipment, set up a reaction apparatus as illustrated in the attached scheme. Securely clamp the still flask and all other parts of the apparatus to a sturdy lab-stand or support rod.
6. Make sure that there is an ample supply of nitrogen or argon that will last at least 24 hours with a slow rate of bubbling and establish that both nitrogen/argon and cooling water are flowing at a reasonable rate with the hose connections to the condenser secured by copper wire or similar.
7. If the solvent still contains **sodium or potassium**:
  - a) With stirring, slowly add an equal volume of toluene or preferably xylene to the flask (see attached figure) while maintaining a slight counter-flow of nitrogen or argon through the apparatus. The counter-flow should be maintained during any additions to the flask throughout the entire procedure. Stir for 5-10 min. observing the reaction.
  - b) With stirring, add 1 ml of n-butanol or t-butanol and observe the reaction. In the presence of active metal hydrogen gas evolution will occur. Further 1 ml portions of the alcohol are added at such a rate that the heat evolved by neutralization does not cause the reaction mixture to come to reflux. This will take several hours, or even longer. The reactivity of the mixture can be monitored by briefly interrupting the nitrogen flow and monitoring the bubbler. As long as there is gas evolution from the apparatus, reactive metal is present.
  - c) When no further reactivity is observed, procedure b) is repeated with ethanol. Again this may take several hours, or overnight, until all hydrogen evolution ceases.
  - d) Add 50-100 ml methanol in 5 ml portions and monitor the reaction. Stir at least 1 h or until no further gas evolution is observed.
  - e) Repeat procedure b) with water until no further gas evolution is observed.
  - f) Dispose of the contents of the flask as organic chemical waste from your laboratory.
8. If the solvent still contains **lithium aluminum hydride**:
  - a) With stirring, slowly add 1 ml portions of 95 % ethanol to the flask containing the hydride in solution (see attached figure) while maintaining a slight counter-flow of nitrogen or argon through the apparatus. The counter-flow should be maintained during any additions to the flask throughout the entire procedure. Stir for 5-10 min. observing the reaction. When no more gas evolution is

observed slowly add a saturated solution of ammonium chloride.

- b) Separate the organic and aqueous layers formed.
  - c) Dispose of the two components in the appropriate manner, i.e., the organic layer into the organic waste collection container, the aqueous layer into the aqueous waste collection container in your laboratory.
9. If the solvent still contains **calcium hydride in dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>)**:
- a) With stirring, slowly add 1-2 ml portions of methanol to the flask (see figure) while maintaining a slight counter-flow of nitrogen or argon through the apparatus.
  - b) The counter-flow should be maintained during any additions to the flask throughout the entire procedure. Stir for 5-10 min. after each addition observing the reaction.
  - c) When no more gas evolution is observed slowly add excess water.
  - d) Separate the organic and aqueous layers formed.
  - e) Dispose of the two components in the appropriate manner, i.e., the organic layer into the halogenated organic waste collection container, the aqueous layer into the aqueous waste collection container in your laboratory.



### 3.15.3. Column Purification Systems

Commercially available column purification systems are a viable alternative for some distillation procedures. While the column method does not have the fire or explosion initiators that distillation units have, they do, however, have their own set of safety considerations that must be accounted for.

1. The quantities of solvents in the system tend to be larger so the units must be used in an appropriate location equipped with flammable liquid cabinets, fire doors, sprinklers, and the quantity limits imposed by the building codes must not be exceeded.
2. The columns are pressurized from 5-50 psi therefore; they must be secure and equipped with the appropriate valves and plumbing.
3. Peroxides may accumulate on the columns and must be changed in accordance with the manufacturer's recommendation.
4. Some solvents, including tetrahydrofuran and methylene chloride, are incompatible with the copper catalyst therefore; the column method may not be suitable for some applications.

References: Cournoyer, Michael E., and Dare, Jeffery H., The Use of Alternative Solvent Purification Techniques, *Chemical Health and Safety*, July/August, 2003.