Guidelines and Standard Operating Procedure (SOP) for the Set-up, Use, and Neutralization of Solvent Stills Containing Reactive Metals or Metal Hydrides.

Solvent stills in which flammable liquids are purified by distillation from reactive metals or metal hydrides such as Na, Mg, CaH_2, or $LiAlH_4$ possibly pose the greatest danger in any organic, organometallic, or inorganic synthetic 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 enormous and the effects on personnel and equipment of a solvent still on fire within the enclosed space of a laboratory are best likened to those of a Molotov cocktail. The chances of personnel escaping such an incident unharmed are very low.** An accident, that occurred at the University of Western Ontario/London several years ago during an attempt to neutralize a sodium containing solvent still, killed one post-doctoral researcher and severely injured a student (3^{rd} degree burns to large parts of the body).

In light of these hazards the safety committee mandates that the following recommendations and standard operating procedures should be followed:

1) Any solvent stills containing reactive metals should be located in a fume-hood.

2) The total volume of solvent used in these stills shall be kept to a minimum.

3) Stills should be operated under an inert gas atmosphere of nitrogen or argon.

4) Types of drying agents recommended

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 $LiAlH_4$ must never be heated. As a drying agent $LiAlH_4$ is therefore only suitable for non-reducible solvents that can be obtained pure by flask-to-flask vacuum-transfer at ambient temperature.

The use of potassium alone is recommended for THF only – in this 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).

The use of sodium alone is recommended for diethylether and all other hydrocarbons such as toluene, benzene, pentane, hexane, heptane, etc.

Calcium hydride is recommended for methylenechloride.

Magnesium/Iodine is recommended for methanol and ethanol.

For all high boiling solvents the use of 4 Å molecular sieves (activated by heating under full dynamic vaccum overnight) is recommended.

5) Solvent stills should never be left running (i.e. being heated to reflux) while unattended – especially not overnight.

6) Stills should be deactivated and restarted on a regular basis to avoid buildup of metal hydroxides and benzophenone Acakes@ that would impair stirring necessary during deactivation.

7) The attached SOP should be followed when deactivating a solvent still containing reactive metals.

Further information about solvent purification can be found in:

a) "Purification of Laboratory Chemicals"

D.D. Perrin & W.L.F. Armarego, Pergamon Press

(This book is available in several synthetic labs, including Tam, Schlaf, and Lange).

b) University of Guelph – Safety Policy Manual

SOP: Neutralization of solvent stills containing reactive metals or metal hydrides.

People have died doing this the wrong way - so please read and follow these procedures carefully and take your time !
Only properly trained persons are to perform this procedure.

1) Notify your lab-mates and supervisor of your intent to perform this procedure. **Do not perform this procedure "after-hours".**

2) Wear a lab-coat, safety glasses, face-shield, and gloves. Orient yourself as to the location of the nearest emergency shower, fire blanket, and exit. Have a dry-chemical fire-extinguisher available.

3) 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 do the trick stop and seek assistance from your supervisor.**

4) 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.

5) Make sure that there is an ample supply of nitrogen or argon that will last at least 24 h 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.

6) 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 reaction mixture is kept just below its reflux temperature. **This will take several hours.** 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.**

d) Add 50-100 mL methanol in 5 mL portions and monitor the reaction. Stir at least 1 h and then until no further gas evolution is observed.

e) Repeat procedure b) with water until no further gas evolution is observed.

d) Dispose of the content of the flask in the organic waste collection container in your laboratory.

7) 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.

b) When no more gas evolution is observed slowly add a saturated solution ammonium chloride.

c) Separate the organic and aqueous layers formed.

d) 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.

8) If the solvent still contains calcium hydride in CH_2Cl_2:

a) With stirring slowly add 1-2 mL portions of methanol 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. after each addition observing the reaction.

b) When no more gas evolution is observed slowly add excess water.

c) Separate the organic and aqueous layers formed.

d) 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.

Schematic reaction apparatus for the neutralization of solvent stills containing reactive metals.

MUST BE SET-UP IN FUMEHOOD !!!