

Rubin's group laboratory operating procedure series

3. Quenching Solvent Drying Still Bottoms

REVISION RECORD

Rev.#	Date	By	Description
1	August 29, 2009	Robert Kennedy	Initial release

APPROVED

(Signature and date on file)

PI/date

(Signature and date on file)

Group Safety Manager/date

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1. PROCESS: QUENCHING SOLVENT STILL DRYING BOTTOMS

The process of quenching solvent drying still bottoms is very dangerous. If not handled properly, fire or explosion can result. The steps and information outlined below must be followed while quenching solvent drying still bottoms. Consult your Principal Investigator before modifying these steps. This document is to serve as a guide for the safe quenching of solvent drying stills. Reading this guide does NOT mean the completion of the required laboratory safety training. Only qualified members should ever attempt to quench a solvent drying still.

When a distillation flask becomes discolored and filled with a brown semi-solid material, it is time to start over with new solvent and drying material (usually sodium or lithium metal or a metal hydride). However, one must first ‘quench’ the old flask. The quenching procedure should be performed as soon as possible to avoid the possible production of peroxides in the solvents. It is good policy to quench these strong bases in a timely fashion so someone else will not be injured by negligence. Do not let the drying agents sit for weeks in the fumehood for passive quenching as this may result in the formation of peroxides. Also, it is extremely important not to rush the quenching process so allocate plenty of time for the process.

Proceed very slowly and cautiously with the successive addition of the alcohols (described below) and employ manual agitation from time to time. Be especially cautious if the drying agent is coated with tar. The key thing to remember when quenching a solvent still is to be VERY PATIENT. The reaction can take a few minutes to get going, and the addition of too much quenching solvent too quickly can cause a runaway reaction to occur. Often, when killing a large still with tar-coated drying agents, it is safer to let the reaction run overnight with alcohol.

1.1 Quenching Steps

First of all, make sure of the following things.

- The quenching operation will be always performed in a properly operating fume hood.
- There must not be any other flammables or explosives stored in the fumehood at the time of quenching.
- Have the appropriate fire extinguisher ready and refresh your memory on how to use it.
- Never perform this process alone; there **MUST** be another person in the lab who is aware of the situation, is familiar with the standard operating procedure, and is prepared to deal with an emergency. Ideally, the process should be directly supervised by lab mate.

1) First, separate extremely flammable solvents like ether away from the drying agent by decanting or by distilling while the flask is connected to the still. Remove the flask to a clean, clear fume hood. Make sure that the fumehood is clear of all flammables and unnecessary equipment. Acquire a labeled container in which to place the unused portion of the solvent to be dried. If this is to be discarded, then it must first be properly labeled as hazardous waste.

2) Decant the bulk (NOT all) of the remaining solvent into the appropriate labeled container. (CAUTION: avoid exposing the drying agent to air.) Secure the flask with a clamp and ring stand if necessary to prevent it from falling over. Keep the solution stirred either mechanically or by a spark-proof magnetic stirrer. Aim the mouth of the flask away from any people or equipment. If you are quenching a large volume of metal/hydride, obtain and use a blast shield.

3) Use a pipette to add a small aliquot (1 mL) of *iso*-propanol. Perform the entire quenching operation under argon. If bubbles of gas appear, wait until they stop, then add another small aliquot of *iso*-propanol. Continue this cautious stepwise addition until the generation of gaseous bubbles becomes very slow.

4) After the *iso*-propanol, and using the same stepwise approach, cautiously add ethanol in small portions (1 mL) 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.

5) After the ethanol addition, add water dropwise and cautiously, pausing between drops for the generation of gas bubbles to slow.

Be very careful with the addition of water. Even after ethanol has been added, the drying agent can still react violently with water, especially if there hasn't been sufficient mechanical stirring of the solution. Mechanical stirring is vital because water is relatively dense and immiscible. It will sink to bottom and react vigorously with the remaining solid.

6) Once the reaction with water is complete, add citric acid solution to neutralize the basic solution. Add the acid in aliquots with the goal of obtaining a pH of between 5 and 9. Pour this solution into a properly labeled waste container and see that it is disposed of in a safe, legal manner. 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.

2. HAZARDOUS CHEMICALS INVOLVED

FLAMMABLE LIQUIDS:

Glyme (1,2-Dimethoxyethane or ethylene glycol dimethyl ether), THF (tetrahydrofuran), diethyl ether (ether or ethyl ether), dioxane (1,4-dioxane or *p*-dioxane), toluene, hexanes, *p*-xylene, acetone, pyridine,

DMF (dimethylformamide), acetonitrile, chloroform, diisopropyl amine, triethyl amine, diisopropyl ethylamine, diphenyl ketone (benzophenone), triethylamine, *n*-pentane, benzene, *iso*-propanol, ethanol

Notes:

1) The ethers (glyme, THF, ether, dioxane) can form explosive peroxides when exposed to air and stored for an extended period of time.

2) Some of these chemical are 'Known to the State of California to Cause Cancer' including benzene and 1,4-dioxane.

TOXIC LIQUIDS:	Glyme
CORROSIVES:	Calcium hydride, sodium, lithium, pyridine
FLAMMABLE SOLIDS:	Sodium, lithium, calcium hydride
ACIDIC SOLIDS:	Citric acid
CAUSTIC SOLIDS:	Sodium, lithium, calcium hydride
ACIDIC LIQUIDS:	Aqueous solution of citric acid

3. PERSONAL PROTECTIVE EQUIPMENT

EYE PROTECTION: Safety Glasses or Goggles, Face Shield if desired

PROTECTIVE CLOTHING: Lab coat. An apron may be worn over the lab coat.

Gloves: nitrile, butyl, PVC or relevant material

4. ENGINEERING / VENTILATION CONTROL

Use a fume hoods, preferably with the sliding sash windows. Perform all operations in the hood, stand behind the sliding safety screen and reach around to perform the manipulations required.

5. SPECIAL HANDLING PROCEDURES AND STORAGE REQUIREMENTS

Label the hazardous materials with their full name (*i.e.* tetrahydrofuran not THF). Store the flammables in the approved flammables storage cabinet. Use secondary containment carriers whenever transporting hazardous material outside of the lab. Use due care and caution when moving hazardous materials around anywhere.

6. SPILL AND ACCIDENT PROCEDURES

Before attempting to quench a solvent still bottom, read the standard operating procedure (SOP) for the correct response to a chemical spill.

A fire extinguisher and spill kit should be close to hand.

If the unquenched flask is spilled, move quickly and carefully away. The drying agent may spontaneously ignite in the air and the flammable solvent may cause a flash fire. Inform EVERYONE in the immediate area and have them move to safe location.

If the spill is large, call the hazardous materials response spill team and inform them of the condition. There are two likely occurrences: (a) The flammable solvent will evaporate and the alkali metal or metal hydride will oxidize with the moisture in the air. (b) The alkali metal or metal hydride will react vigorously with a proton source (like water) and will generate hydrogen gas, which may spontaneously ignite with the heat of the reaction. In the event of a large fire, EXIT IMMEDIATELY and CALL the FIRE DEPARTMENT (911).

If the spill is small, and doesn't contain any alkali metal or metal hydride, treat it as a flammable materials spill and 'dike' it with absorbent spill cleanup material (vermiculite, sand, polypropylene, silicates) cover the spill with the absorbent then, once the spill is absorbed, sweep it into a bag, properly labeled with the contents for hazardous waste disposal. A small fire may be dealt with using the appropriate fire extinguisher.

If the spill evaporates completely and leaves the slowly oxidizing alkali metal or metal hydride behind, gather these carefully into a beaker and quench with the previously described procedure.

7. WASTE DISPOSAL

Dispose of the properly labeled hazardous waste in a safe legal manner. Non-hazardous waste may be placed in a container to go to a sanitary landfill or, if appropriate, washed into the sewerage system.