

Quenching Reactive Metal Still Bottoms

Standard Operating Procedure

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PROCESS (see spill procedures for emergency response)

When a distillation flask becomes discolored and filled with a brown semi-solid. It is time to start over with new solvent and drying material (usually sodium or lithium metal or a metal hydride.) One must first 'quench' the old flask. This procedure should be performed as soon as possible to avoid the production of shock-sensitive explosive crystals in those solvents that are prone to peroxide formation. Also it is good policy to quench these strong bases in a timely fashion so someone else will not be injured.

The Procedure:

1. First, remove the flask to a clean, clear fume hood. 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. Obtain a container of sufficient size to hold both ice water and the flask.
2. Next, decant the bulk of the remaining solvent into the appropriate labeled container. NOTE: If the still was neglected and there is a ball of metal surrounded by tar, it would be wise to make sure that there is a high boiling inert solvent (e.g. xylene) to keep the drying agent covered at all times and to act as a heat sink in case of sudden reaction. Place the flask into the ice water bucket, secure it with a clamp and ring stand if necessary to prevent it from falling over. Aim the mouth of the flask away from any people or equipment. If you feel uncomfortable, or are quenching a significant volume of metal/hydride, obtain and use a blast shield.
3. Now, use a pipette to add a small aliquot of sec-butanol. (If you wish to work with an added layer of safety, perform the entire quenching operation under argon or nitrogen gas.) If gaseous bubbles appear, wait until they stop, then add another small aliquot of sec-butanol. Continue this cautious step-wise addition until the generation of gaseous bubbles becomes very slow.
4. After the s-butanol, try adding an alcohol with more freely available protons, like n-butanol. Continue the same cautious, step- wise approach 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. Once you've used n-butanol, try the same step-wise cautious addition with these solvents in sequence: isopropanol, ethanol, methanol and water.

5. Be Very Careful with the addition of WATER! Even after methanol has been added, the drying agent can still react violently with water, especially if there hasn't been sufficient mechanical stirring of the solution. So add in small aliquots.
6. Once the reaction with water is complete, use a suitable acid solution to neutralize the basic solution you've created. Good choices include 3 molar hydrochloric acid (3 M HCl) and citric acid, which may be easier to use. Add the acid in aliquots with the goal of obtaining a pH of 7. Don't be obsessive about this obtaining this exactly; in the 5 - 9 range is OK. 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.

APPROVAL REQUIRED

BEFORE conducting this operation, approval from the Principal Investigator, or designated person, is REQUIRED.

HAZARDOUS CHEMICALS INVOLVED

For Chemical Safety Information review the Material Safety Data Sheets for the materials with which you are working

FLAMMABLE LIQUIDS:

Notes:

1. The ethers (glyme, THF, ether, dioxane) can form explosive peroxides when exposed to air and stored for a time.
2. Some of these chemicals are known, or anticipated to be carcinogenic www.osha.gov/SLTC/carcinogens, including benzene and 1,4-dioxane.
 - GLYME (1,2-Dimethoxyethane or Ethylene glycol dimethyl ether)
 - THF (Tetrahydrofuran)
 - Et₂O (Ether, or Diethyl ether, or Ethyl ether)
 - Dioxane (1,4-Dioxane or p-Dioxane)
 - Pentane
 - Benzene
 - sec-butanol
 - n-butanol
 - isopropanol
 - ethanol
 - methanol

CORROSIVES:

ACIDIC SOLIDS:

- Citric acid

CAUSTIC SOLIDS:

- Sodium
- Lithium

ACIDIC LIQUIDS:

- Hydrochloric Acid

PERSONAL PROTECTIVE EQUIPMENT

EYE PROTECTION

- Chemical Safety Goggles (or Safety Glasses if there is no splash hazard)
- Face Shield if desired

PROTECTIVE CLOTHING

- Apron or Lab coat (Flame resistant coat proffered)
- Gloves: nitrile, butyl, PVC or relevant material

ENGINEERING/VENTILATION CONTROLS

Use a fume hood, preferably with the sash as closed as possible and a blast shield. Perform all operations in the hood, stand behind a blast shield (or the sliding sash windows – if so equipped) and reach around to perform the manipulations required.

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.

SPILL and ACCIDENT PROCEDURES

- If one spills the unquenched flask, MOVE QUICKLY 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, the flammable solvent will evaporate and the alkali metal or metal hydride will oxidize with the moisture in the air. Or 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. If this occurs, EXIT and CALL the FIRE DEPARTMENT, the entire area may be quickly engulfed in flames.
- 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 (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.
- 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 same previously described procedure.

WASTE DISPOSAL

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

DECONTAMINATION

All contaminated personal protective equipment and glassware used should be washed with soap (or detergent) and water.

DESIGNATED AREA

The operation should ONLY BE CONDUCTED in a CLEAN, Properly Operating FUME HOOD. DO NOT perform this process ALONE! Have an informed, prepared person be in the area.

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