



# Department of Chemistry

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## Safety - Standard Operating Procedures - Solvent Stills

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### Solvent Stills

The principle purpose of solvent stills is to provide a source of pure, completely dry solvent with a minimum of lead time. Whether or not a solvent requires a permanent, recycle type still or a more temporary solution depends on both the volume and frequency of its use. Several different varieties of still heads are commercially available. For permanent setups the best designs can be set to recycle rather than to collect solvent. This would allow the stills to be kept permanently hot rather than having to be started from room temperature each time distilled solvent is needed. It is very important in this type of still to size the receiver vessel appropriately to the still-pot. The receiver should never be more than half the size of the still-pot. For commonly used solvents, two and five liter still-pots are the most commonly used. Solvents used in lesser quantities can be dispensed from smaller stills; but stills smaller than about 250 mL are, in most cases, more trouble than they are worth. The still-pot should always have at minimum two necks; otherwise the still will have to be taken apart to add fresh solvent or drying agent. To keep stills dry and oxygen free, they are connected to an inert gas source, and fitted with a bubbler to vent excess pressure.

Among the first decisions to be made is whether to use argon or nitrogen as the inert gas. Nitrogen is cheaper and house nitrogen is generally pure and dry enough for stills. Argon, being denser than air, has a better blanketing effect, but it is more expensive and generally only available in cylinders. Nitrogen is probably the best choice in most cases as the permanence of a house supply means the stills will not be deprived of inert gas by a cylinder being emptied over a long weekend.

The use of a sodium benzophenone ketyl solution is among the most common methods to prepare pure, anhydrous, oxygen-free solvents. The use of a ketyl solution is, of course, restricted to solvents that do not react with the alkali metals. Suitable solvents include various ethers and hydrocarbons.

Chlorinated solvents, and solvents subject to reduction such as dimethylformamide, dimethylsulfoxide and acetonitrile, should be dried with calcium hydride.

The question of whether to use potassium or NaK versus sodium in ketyl stills is a common conundrum. Potassium (m.p. 64°) and NaK have lower melting points and thus tend to form their ketyls more easily (fresh metal surface is continually being exposed to the benzophenone solution). However, a sodium ketyl, once formed, is just as capable as the others in preparing dry and oxygen free solvents. It also has the advantage of being much more simply and safely disposed of. In the case of solvents like toluene and xylenes that boil above sodium's melting point (m.p. 98°) there is no question that they will be dried quickly and thoroughly by sodium. The most commonly used

solvents and how they should be purified are listed below:

**Diethyl ether**, b.p. 34.6°

Ether from freshly opened cans can be added directly to a ketyl pot. Sodium metal (5 g per liter of solvent) should be cut into roughly 5 mm cubes, first under hexane to remove adhering oil and then transferred to a small bath of ether to wash away any hexane, and finally transferred to the ketyl pot. Benzophenone (10 g per liter) is then added and the solution heated to reflux. Diethyl ether's ketyl is a deep royal blue. If, after refluxing for twenty minutes, the still-pot is not permeated by the dark blue of the ketyl, more sodium is needed. Cool the still-pot to room temperature and carefully add a few more pieces of metal, then reheat.

**Tetrahydrofuran**, b.p. 65.4°

As THF is completely miscible with water it is best not to take any chances as to it being wet. THF should be first refluxed 24 hours over calcium hydride (10 g per liter) then distilled for use in the ketyl pot. Sodium preparation is similar to that for diethyl ether, the final wash of course would be with THF. THF's ketyl is a deep purple color.

**Benzene**, b.p. 80.1°

**Toluene**, b.p. 110.6°

**Xylenes**, b.p. 138-144°

These aromatic solvents, from freshly opened bottles, can be added directly to a ketyl pot. No pretreatment of these solvents is necessary. Sodium and benzophenone amounts should be as for diethyl ether. Ketyl color will be dark blue to purple. Be sure to leave plenty of expansion room in toluene and xylene stills. Their high boiling points and relatively high expansion coefficients can lead to serious problems if not allowed for.

**Pentane**, b.p. 36.1°

**Hexane**, b.p. 68.7°

These hydrocarbons need extensive pretreatment. Either should be stirred for at least one week over concentrated sulfuric acid ((250 mL per L solvent). The acid should be changed as it turns black. Once fresh acid is no longer darkened the hydrocarbon is ready for the next step. Wash twice with water, then carefully wash with saturated bicarbonate. Dry thoroughly over calcium chloride, then add to still. In addition to the sodium and benzophenone, diglyme is necessary to solubilize the ketyl ((10 ml per liter solvent). The ketyls are dark blue after reflux overnight.

**Acetonitrile**, b.p. 82°

Acetonitrile can be used directly from a freshly opened bottle with no pretreatment. Calcium hydride (10 g per liter) is used as the drying agent.

**Dichloromethane**, b.p. 40.0°

Dichloromethane can be used directly from a freshly opened bottle with no pretreatment. Calcium hydride (10 g per liter) is used as the drying agent.

**Dimethylformamide**, b.p. 153°

Calcium hydride (10 g per liter) is used as the drying agent, followed by filtering off the hydride and distillation. Serious decomposition problems occur with acidic or basic drying agents. DO NOT reflux with the calcium hydride. Can be used directly from a freshly opened bottle with no pretreatment.

**Dimethylsulfoxide**, b.p. 190°

Although fully miscible with water, DMSO from freshly opened bottles is dry enough to be used without preliminary drying. Calcium hydride (10 g per liter) is used as the drying agent.

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## Quenching Solvent Stills

The quenching of used still-pots, especially ketyl pots, is potentially dangerous but can be done safely if appropriate precautions are taken. These include: wearing goggles, labcoat and gloves; working in a well ventilated hood behind a safety shield; and quenching the reactive compounds slowly.

Stills that used calcium hydride as the drying agent are the easiest to quench. After the majority of the solvent has been decanted away from the drying agent, the remainder, along with the calcium hydride, is poured slowly over crushed ice. The ice is replaced as it melts so that the unreacted calcium hydride is always being added to a solution that consists mostly of ice. Lumps stuck in the still-pot must be carefully removed with a spatula. When nothing but a thin film of hydride remains in the stillpot it can be washed out with cold water.

Ketyl pots require special care. First, one must be certain as to whether the still had contained sodium, potassium, or NaK. The process is similar for all three; if uncertain, assume potassium is present and use the following procedure:

1. The entire quenching process should be carried out under a steady stream of nitrogen with a large opening to vent both the nitrogen stream and the hydrogen gas which is generated.
2. Pour off excess solvent, and refill the flask with dry xylene or toluene.
3. Add a reflux condenser and an addition funnel filled with sufficient dry tert-butyl alcohol to react with 150% of the expected amount of metal.
4. The alcohol is added dropwise, stopping if the solution begins to boil too vigorously.
5. After the addition is complete, the solution is heated to reflux overnight.
6. The process is repeated with isopropanol and then methanol.
7. If no bubbling is observed upon addition of methanol a small (1 mL) quantity of water is added to confirm that all of the metal has been quenched. If the still only used sodium the tert-butyl alcohol step may be omitted and the process may be begun with isopropanol. The final mixture may be safely disposed of in a hazardous waste container.

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