

DISTILLATION OF SOLVENTS

Hazards

The primary hazard arises from the solvent's property of being highly or extremely flammable but several are also described as harmful and/or toxic.

Flammable hazards. The most common fire hazard in the laboratory is a flammable liquid or the vapour produced from such a liquid. For a fire to occur requires i) an oxidising atmosphere (usually air), ii) flammable gas or vapour at a concentration within the flammability limits of the substance and iii) a source of ignition. Under normal circumstances oxygen or air will always be present and the optimal way to prevent fire is to segregate the vapour or gas from sources of ignition.

With distillation, a specific chemical drying agent is used for each solvent, which may react violently with other solvents. Particularly dangerous in this respect are sodium and lithium aluminium hydride.

Risks

Solvents are in constant use and the risk of fire is always significant with all the dangers that entails to personal safety and property damage. The level of injury could range from minor burns to death.

Risks should normally be low if the rules below derived from experience are followed carefully, the stills are constructed to the standard design and sources of ignition are controlled. However, distillation does involve risks and an important first question must be do you really need a solvent still? Can you use commercial dried solvent or share a still?

Training

New users have to contact the responsible for the solvent stills as stated on the labels for each still for assistance (and evt training in the use of the still).

Recommendations for Solvent Still Operation and Construction

1. Location of Stills

- Solvent stills are potentially dangerous and should be located in the fume hood at C433 dedicated to this purpose.

2. Water Supply

- All water connections, from the tap to the still and from the still to the drain, are to be secured using nylon or metal ties.
- Water tubing to be made of a material such as translucent polyvinyl chloride, which is resistant to perishing.
- Make sure that sufficient water pass through the coolers.

3. Nitrogen Supply and Vent

- On no account must it be possible to seal off a still from its vent and so create a pressurised system.
- Each still must have its own individual nitrogen supply and bubbler.
- Flexible connections are to be made using translucent polyvinyl chloride tubing, and to be secured using a nylon or metal tie to the supply valve, the still 'Tee' pieces and the bubbler.
- Flexible connections in the case of a tetrahydrofuran still should be made from polytetrafluorethylene tubing, which is resistant to this solvent.
- All exit tubing has to be attached so as to minimise the danger of kinking and vented to a fume hood or the exterior of the building.

4. Electricity Supply

- The electricity supply at the fume hood has to be controlled by a key (hold by the responsible for the solvent stills as stated on the labels) and a timer.
- The timer is never to be set to more than 3 hours of electricity supply.

5. Miscellaneous

- All still flasks must be labelled in plain English, no chemical shorthand, stating the solvent and the drying agent.
- Sand (for Na) and vermiculite (for solvents) should be available near by the solvent still in case of minor spillage.
- Never collect solvents when the flask is less than half full.
- Stills have to be turned off when left unattended.
- The joint between the still flask and the receiver must be fitted with a heavy duty PTFE joint sleeve.

6. Recommended Solvent Drying Agents

Solvent	Drying Agent
Tetrahydrofuran	Sodium/benzophenone
Ethanol	Magnesium
Acetonitrile	Calcium hydride
Acetone	Calcium chloride
Dichloromethane	Calcium hydride
Ethyl acetate	Calcium hydride
(2-Methoxyethyl)ether	Sodium
40/60 Petrol ether	Calcium hydride or Sodium/benzophenone/triglyme
Toluene	Sodium
Diethyl ether	Sodium/benzophenone
Methanol	Magnesium
Hexane	Calcium hydride or Sodium/benzophenone/triglyme
Pentane	Calcium hydride or Sodium/benzophenone/triglyme
Heptane	Calcium hydride or Sodium/benzophenone/triglyme
Benzene	Calcium hydride or Sodium
Xylene	Sodium

This list is not exhaustive. The routine use of potassium or its alloys is not recommended because of the risk of fire; if potassium must be used, a special assessment has to be made with particular concern for its disposal.

7. Hazardous Reactions

For a comprehensive list of hazardous reactions associated with drying agents check "Hazardous Laboratory Chemicals Disposal Guide" available at C4xx.

Sodium

- *Acids.* Anhydrous hydrochloric acid, hydrogen fluoride, or sulfuric acid react slowly with sodium while aqueous solutions react explosively
- *Air.* Dispersions of sodium in volatile solvents become pyrophoric if the solvent evaporates round the neck of a flask; serum cap closures are safer.
- *Ethanol.* Air must be excluded when reacting finely divided sodium with ethanol to avoid hydrogen-air mixture explosions.
- *Halocarbons.* Sodium in halocarbons forms shock and impact sensitive mixtures.
- *Halogens.* Ignites in fluorine gas and in moist chlorine; mixtures with halogens are shock sensitive.
- *Non-metal halides.* Vigorous or explosive reactions occur with PBr₃ on addition of drops of water, PCl₃, PCl₅, Se₂Cl₂, SCl₂, BBr₃, SBr₂, POCl₃, SOCl₂, SiCl₄ and SiF₄.
- *Non-metal oxides.* Mixtures with solid CO₂ are impact sensitive and explode violently. **CO₂ is unsuitable as an extinguishant.** Finely divided silica will often react with burning sodium so it is not suitable as an extinguishant.
- *Oxygenated compounds.* Mixtures of sodium with inorganic oxygenated compounds of oxygen-rich organic compounds are shock sensitive explosives.
- *Hydrazine. Mercury. Metal halides. Metal oxides. Nonmetals (C, S, Se, Te). Sulfides. Water.*

Calcium hydride

- *Manganese dioxide. Metal halogenates. Silver halides. THF. Water.*

8. Start and Re-fill of Solvent Stills

Use of sodium/benzophenone:

- All flammable solvent stills must only be filled or re-filled when they are at room temperature. There should be no electrical device turned on in the fume cupboard when the still is being filled and all heating devices such as mantles or hotplates must have been turned off for at least 5 minutes to avoid chance ignition of vapour.
- Start drying with approximately 1 g sodium/g water expected and add a small amount (5 g/l) of benzophenone.
- Sodium is cut into thin flakes with a knife on a paper towel to maximize the reactive surface of the sodium.
- To destroy any sodium residues the paper is flushed with a large amount of water in the sink after use.

- Alternatively, small pieces of sodium can be pressed into thin flakes by a glass rod under pentane
- If the colour of the still do not turn deep purple-blue after a day of boiling cool the still to room temperature and add more sodium.
- Repeat if necessary.
- Re-fill or restart when the flask is less then half full.
- Re-fill with solvent of good grade; add more benzophenone and perhaps sodium.
- Keep a log of the amount of sodium used in a still and do not re-fill when the total amount of sodium sums up to 8 g.

9. Safe Disposal of Drying Agents

The reactivity of the above drying agents means that disposal has to be carried out with great care.

- The disposal of drying agents is done in the fume hood in C204. (see also Transport)
- The room is available for Na destruction each Thursday.
- Put the sign "Forsøk pågår" on the outside of the door of C204.
- Wear eye protection, laboratory coat and nitril rubber gloves.
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- Disposal of sodium (10 g or less)

The round-bottom flask from the still is equipped with a stirrer, a dropping funnel and an intensive condenser. Flush the flask with nitrogen. Add isopropanol (about 30 ml per 10 g of sodium) to the dropping funnel with the **tap closed**. The isopropanol is then added slowly to react with the drying agent. There may be a delay in hydrogen evolution whilst surface contamination of the drying agent is dissolved. Start stirring as soon as enough solvent is in the flask to make it feasible. When all sodium is dissolved and the evolution of hydrogen has ceased, a small amount (ca. 15 ml) of a 1:1 ethanol/water mixture is cautiously added. If no further hydrogen evolution occurs, an equal amount of water is cautiously added and the flask is left until no more bubbles of gas can be seen. The flask can now be detached, the upper organic layer separated and put into the waste solvent container and the lower, aqueous layer is neutralized with 6 M sulfuric or hydrochloric acid and washed down the drain with lots of water (take special care with tetrahydrofuran as this is fairly soluble in water).

- Disposal of calcium hydride

The procedure is similar to that used for sodium except that methanol (about 25 ml per 1 g of hydride) is used in place of pure ethanol. When hydrogen evolution ceases, an equal amount of water is added cautiously to the slurry of calcium methoxide. Dismantle when no bubbles can be seen. If an aqueous and an organic layer have formed, these must be separated, the solvent put into the appropriate waste solvent bottle and the aqueous layer is neutralized with 6 M sulfuric or hydrochloric acid, and washed down the drain with lots of water. If the water and solvent are miscible, often the whole

contents of the flask can be washed down the sink with lots of water to render the mixture non-flammable - if you have doubts about what is allowed, check with the "Safety Regulations at the Department of Chemistry".

10. Transport of flask containing drying agents and solvent residues

- Transport of flasks containing flammable solvents and reactive drying agents must be limited to a minimum.
- Use a flask carrier with a holder for round bottom flasks in the bottom and a plate on top to prevent the flask from tilting. To be found at C433.

11. Emergency Procedure

1. Fire:

a) If the fire is clearly minor. Use sand as an extinguisher for fire involving sodium! **Never use a CO₂ extinguisher for fire involving sodium. Do not endanger yourself.** Inform a member of staff.

b) Otherwise: evacuate and close the door. **Operate the nearest fire alarm and turn off the fuse for C433 (U6). Evacuate the building.** Contact a member of staff to advise of the nature of the incident or call 77644199.

2. Spillage, no fire.

a) Serious - toxic or large quantities. Evacuate and close the door. **Operate the nearest fire alarm and turn off the fuse for C433 (U6). Evacuate the building.** Contact a member of staff to advise of the nature of the incident or call 77644199. **Do not attempt to clean up major spillage by yourself.**

b) Minor. Beware of drying agent! Use sand to cover sodium to prevent exposure to air or water. Shut down the electricity of the fumehood in C433 by turning off the fuse (U6 T7). Inform a member of staff and your co-workers. Decide on and use suitable protective equipment such as gloves, lab. coats, respirators. Solvent may be absorbed onto vermiculite and, as appropriate, transferred to a fumehood to evaporate or to a suitable sealed container for waste disposal. In a well-ventilated area such as a laboratory, the best procedure may be simply to turn off sources of ignition, ventilate, evacuate and seal and secure the room.

3. Personal injury.

"Safety Regulations at the Department of Chemistry"

3. Flood.

If it is obvious, stop the leak. Warn people in the rooms below to safeguard papers and equipment. **Do not attempt to move wet electrical equipment until it is disconnected from the mains.** Inform members of staff.