

## Drying Solvents:

Note: When the solvent is to be distilled after standing over a desiccant, the drying agent should be filtered off before distillation if it removes water reversibly, e.g. by hydrate formation ( $\text{MgSO}_4$ ,  $\text{CaCl}_2$ ), or by absorption (molecular sieves). The solvent can be distilled without removal of the desiccant in cases where water removal is irreversible ( $\text{CaH}_2$ ,  $\text{P}_2\text{O}_5$ ).

## Drying agents:

- **Alumina,  $\text{Al}_2\text{O}_3$**   
Neutral or basic alumina of activity grade I is an efficient drying agent for hydrocarbons, 5% w/v loading giving extremely dry solvents. It is also useful for the purification of chloroform and removal of peroxides.
- **Barium oxide,  $\text{BaO}$**   
The commercially available anhydrous product is an inexpensive drying agent which is useful for amines and pyridines (30-50ppm after standing for 24 hours over 5% w/v). It is strongly basic and is ineffective for alcohol and dipolar aprotic solvents.
- **Boric anhydride,  $\text{B}_2\text{O}_3$**   
Recommended drying agent for acetone, and effective also for thorough drying of acetonitrile.
- **Calcium chloride,  $\text{CaCl}_2$**   
Both the powder and pellet forms are effective for pre-drying hydrocarbons and ethers. It reacts with acids, alcohols, amines and some carbonyl compounds.
- **Calcium hydride,  $\text{CaH}_2$**   
The reagent of choice for rigorous drying amines, pyridines, and HMPA, and effective also for drying hydrocarbons, alcohols, ethers, and DMF. It is available in powdered or granular form; the granular is preferable if it is to be stored for any length of time. The granules should be crushed immediately before use and residues should be destroyed by careful addition of water.
- **Calcium sulfate (Drierite),  $\text{CaSO}_4$**   
It is only suitable for drying organic extracts. The blue self-indicating version should not be used to dry liquids because the colored compounds may leach into the solvent.
- **Lithium aluminium hydride (LAH),  $\text{LiAlH}_4$**   
Although widely used for drying ethers, it is less effective than other methods and is extremely dangerous. Its use is strongly discouraged.
- **Magnesium,  $\text{Mg}$**   
Recommended for methanol and ethanol.
- **Magnesium sulfate,  $\text{MgSO}_4$**   
The monohydrate is fast acting and has a high capacity (forms a heptahydrate), making it the desiccant of choice for organic extracts. It is slightly acidic so care is required with very sensitive compounds. It is not efficient enough to be useful for pre-drying.
- **Molecular sieves**  
There are sodium and calcium aluminosilicates which have cage-like crystal lattice structures containing pores of various sizes, depending on their constitution. They can absorb small molecules such as water, which can fit into the pores. The most commonly used types 3A, 4A and 5A are available in bead or powder form. After activation at 250-320 °C for a minimum of 3h they are probably the most powerful desiccant available.

They can be stored in a desiccator or in an oven at  $>100\text{ }^{\circ}\text{C}$  for a few weeks but they are rapidly hydrated in the air. You can test the effectiveness by placing a few beads in your hand and adding a drop of water- it should be an exothermic reaction. Solvents can be dried by allowing to stand over 5% w/v of sieves for 12 h, decanting, adding a second batch of sieves etc. A solvent should always be decanted from the sieves prior to distillation. 4A beads are recommended for thorough drying of amines, DMF, DMSO, and HMPA (store over 5% w/v). 3A form is suitable for drying acetonitrile, methanol, and ethanol, and higher alcohols require the use of powdered 3A sieves. They are not useful for drying acetone because they cause self-condensation. Sieves can be reused, if not discolored, by washing well with a volatile organic solvent, allowing to dry, drying at  $100\text{ }^{\circ}\text{C}$  for several hours, and then reactivating at  $300\text{ }^{\circ}\text{C}$ .

- **Phosphorus pentoxide,  $\text{P}_2\text{O}_5$**

Although a rapid and efficient desiccant its use is limited by its high chemical reactivity. It reacts with alcohols, amines, acids, and carbonyl compounds and causes significant decomposition of HMPA, DMSO and acetone. It is useful for drying acetonitrile and may be used for hydrocarbons and ethers but is less convenient than other reagents. It is often used in desiccators. IT is best decomposed by careful portionwise addition to ice-water followed by neutralization with base (do not add water to  $\text{P}_2\text{O}_5$ , the mixture may become so hot that the vessel could crack). It is extremely efficient for drying gases and is available in a convenient form, mixed with an inert support, so that it does not become syrupy.

- **Potassium hydroxide, KOH**

freshly powdered KOH is a good drying agent for amines and pyridines but is inferior to calcium hydride. It should not be used with base sensitive solvents.

- **Sodium, Na**

Sodium is widely used to dry hydrocarbons and ethers. It may be formed into wire using a sodium press or as granules by cutting the bars under petroleum ether. It suffers from the disadvantage that the metal surface rapidly becomes coated with an inert material so it should not be used unless the solvent is pre-dried. Sodium reacts with benzophenone to give a dark blue ketyl radical which is protonated by water to give colorless products. Thus the sodium-benzophenone system is particularly convenient because it is self-indicating, and it is the preferred reagent for rigorous drying of diethyl ether, THF, DME, and other ethereal solvents. Sodium-potassium alloy has been recommended because it is liquid and therefore its surface does not become coated so easily, but this advantage is outweighed by the increased danger resulting from the use of potassium. Sodium residues can be destroyed by slow careful addition of ethanol until hydrogen evolution ceases. The mixture should then be stirred well, to ensure that no coated lumps of sodium remain, before carefully adding methanol. After leaving for several hours the mixture should be stirred again to ensure that all of the sodium has been consumed, and then the mixture should be added cautiously to a large excess of water before disposal. Sodium should never be added to a chlorinated solvent because of a vigorous or explosive reaction could occur.

- **Sodium sulfate,  $\text{Na}_2\text{SO}_4$**

Anhydrous sodium sulfate is a weak drying agent suitable only for drying extracts. It is preferable to magnesium sulfate for drying very acid sensitive compounds.

Source: Lenodard, J. *et al.* Advanced Practical Organic Chemistry. 2<sup>nd</sup> ed. 1998: CRC Press.