

Home and dry - drying agents in organic chemistry

Many organic compounds contain trace amounts of water, particularly if prepared on site. In many cases, this is not a problem: anhydrous ethanol, for instance, is rarely used in schools due to its expense.

Ethanol is an interesting example. As is well known from whisky production, ethanol is separated from water by distillation. However, a mixture of ethanol and water forms an azeotrope (a constant boiling point mixture) that boils below the boiling point of ethanol. It contains 95.6% ethanol and its lower boiling point means that it is impossible to get purer ethanol than this by simple distillation.

Despite saying that the presence of water is not usually a problem, there are times when it can cause issues. We came across one of these recently.

The problem with preparing ethyl ethanoate

Following a standard preparation of the ester, ethyl ethanoate, we encountered problems at the final distillation stage. Whilst the literature states that the boiling point range should be 74-79°C we discovered that the main bulk of the liquid was coming off between 69-74°C. A search of the literature showed that formation of azeotropes in the preparation of ethyl ethanoate is a known problem [1] and results in the pure ester being isolated in a low yield. In fact there is a range of azeotropes formed:

- water-ethyl ethanoate bp 70.4°C;
- ethanol-ethyl ethanoate bp 71.8°C;
- water-ethanol-ethyl ethanoate bp 70.1°C.

The first step to minimise the problems in this case is to minimise the formation of azeotropes by removing any excess alcohol and water.



Figure 1 - If there is no water in the liquid, your drying agent will remain as fine grains – like this sodium sulphate.

In our experimental procedure the reaction mixture was first washed with saturated sodium carbonate to neutralise any acid present.

A saturated calcium chloride solution was then added to remove excess ethanol. Finally the extract was dried with a drying agent to remove any water before the final distillation.

Common drying agents are anhydrous inorganic salts that acquire waters of hydration when exposed to moist air or a wet solution. Vogel [2] has advice on drying agents (and indeed much else) a suitable drying agent:

- must not react with the organic compound;
- should have a rapid action and an effective drying capacity;
- should not dissolve appreciably;
- should be as economical as possible;
- should have no catalytic effect in promoting chemical reactions of the organic compound such as polymerisation;
- a large excess should be avoided to keep adsorption losses down to a minimum.

The procedure we were following suggested using anhydrous calcium

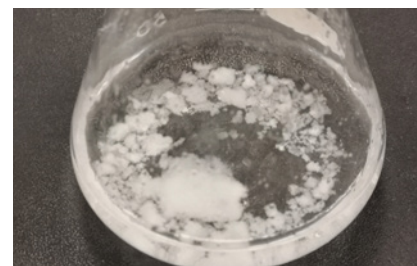


Figure 2 - If there is some water in the liquid, the drying agent will clump together like this.

chloride as a drying agent, however we decided to use anhydrous sodium sulphate.

Being unaware at the time of the problem with azeotropes we suspected that the problem lay with our choice of drying agent and decided to investigate a range of agents to find the best one to remove water from ethyl ethanoate.

We tested 4 common drying agents that would be normally found in a school chemical store:

- anhydrous sodium sulphate (Na_2SO_4)
- anhydrous magnesium sulphate (MgSO_4)
- anhydrous calcium chloride (CaCl_2)
- anhydrous potassium carbonate (K_2CO_3)

The standard method for using drying agents is as follows.

It is preferable to have the wet solvent in a flask.

- 1) Start by adding a small portion of drying agent to the flask and swirling (Figure 1 and 2). *Water causes the drying agent to clump into larger particles (and sometimes stick to the glass).* >>



Figure 3 - Wet solution now dried.

- 2) Add further portions of drying agent until the swirling just shows some particles of the original size swirling round as well as the larger clumps (Figure 3).

You will need to leave the solvent standing on the drying agent for a while to allow the water all to be absorbed.

- 3) Decant or filter the solvent to remove the drying agent.

Once we had dried the solvent, it was then distilled. For these results see Table 1.

Drying agent (all anhydrous)	% original volume collected below 74°C
Na ₂ SO ₄	32-40
MgSO ₄	12-15
K ₂ CO ₃	3-9
CaCl ₂	0

Table 1

So in this particular case it is clear that we made an error in thinking that the drying agent made little if any difference. Calcium chloride is clearly the best and much better than the sodium sulphate we used.

Drying agents more generally

A summary of the properties of the four drying agents is shown in Table 2 [3].

Suitable drying agents [4]

While there are exceptions, general guidance on suitable drying agents can be found Table 3.

Calcium Chloride is a very good drying agent for a wide variety of solvents. It is generally not suitable for compounds containing hydroxy groups, amino groups and carbonyl groups though there are exceptions – such as ethyl ethanoate.

Substance	Capacity	Speed	Intensity
Calcium Chloride	High	Medium	High
Magnesium sulphate	High	High	Medium
Potassium carbonate	Medium	Medium	Medium
Sodium sulphate	High	Low	Low

Table 2 - Capacity refers to the numbers of moles of water that the drying agent can bind. Speed is self-explanatory. Intensity refers to the 'dryness' of the final solution.

Class of compounds to be dried	Recommended drying agent
Alkane, alkyl halides	MgSO ₄ , CaCl ₂
Aromatic hydrocarbons, ethers	MgSO ₄ , CaCl ₂
Aldehydes, ketones	Na ₂ SO ₄ , MgSO ₄ , K ₂ CO ₃
Esters	Na ₂ SO ₄ , MgSO ₄ , K ₂ CO ₃ , CaCl ₂ (not all esters)
Alcohols	MgSO ₄ , K ₂ CO ₃
Amines	K ₂ CO ₃
Acidic compounds	Na ₂ SO ₄ , MgSO ₄

Table 3

Magnesium sulphate is suitable for drying most organic compounds. It works well in solvents like diethyl ether, but not as well for ethyl ethanoate. It is more rapid (partly because it comes as a very fine powder with a large surface area) and more effective than sodium sulphate.

Potassium Carbonate is often used to dry basic solutions containing amines. It cannot be used to dry acidic compounds.

Sodium Sulphate has a very high capacity, but drying is inefficient and slower compared to magnesium sulphate. It is very efficient in ethereal solutions.

Other drying agents

Calcium sulphate is a generally good drying agent but it does not have a high capacity, which makes it useless for very wet solutions.

Potassium hydroxide can be used in place of potassium carbonate but it is significantly more corrosive.

Concentrated sulphuric acid and **phosphorous pentoxide** are both acidic drying agents that are mainly used in desiccators and not in direct contact with the solution since they are very aggressive reagents.

Molecular sieves are aluminosilicates with a three-dimensional network with different pore sizes. They have to be activated prior use but also can be regenerated quite straightforwardly by heating.

Sodium - sodium wire (or similar small pieces) can be used to remove water from solvents by reacting with it. There are obvious hazards associated with this method and it should be avoided unless there is no other option.

Drying gases

These pose a different (though related) challenge. Further information can be found on the [SSERC website](#).



References

- [1] EC Wagner, E.C. (1950), Ethyl Formate, n-Propyl Formate, and n-Propyl Ethanoate Journal of Chemical Education 27 (5), 245.
- [2] Arthur Vogel - Textbook of Practical Organic Chemistry.
- [3] University of Calgary – Organic Laboratory Techniques 7 – Drying Agents, available at <http://www.chem.ucalgary.ca/courses/351/laboratory/drying%20agents.pdf>.
- [4] UCLA - Drying agents, available at <https://www.chem.ucla.edu/~bacher/Specialtopics/Drying%20Agents.html>