

- **RECRYSTALLISATION**



Never heat organic solvents with a Bunsen burner. Use a hot plate or a hot water bath on a hot plate.

The purification of a solid by recrystallisation depends upon the fact that different substances have different solubilities in different solvents. In the simplest case, the unwanted impurities are much more soluble than the desired compound. The impure sample is dissolved in the **minimum volume of hot solvent** to form a saturated solution, then as the solution cools slowly, crystals of the desired compound form and can be collected by filtration. The soluble impurities remain in cool solution and so pass through the filter paper with the solvent.

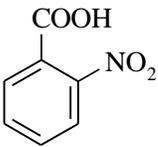
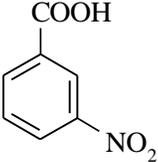
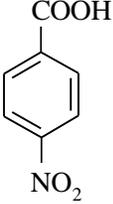
a. **Choice of Solvent**

If you are following a procedure, you will likely be told what solvent to use. However, if that is not the case, then you need to find the right solvent. The choice of solvent is **critical** to the purification by recrystallisation, but there is no simple way to know which solvent will work best. However, some general principles of solubility will assist in this choice. Crystallisation depends primarily on solubility relationships. In most cases the solubility of a compound in any solvent increases markedly with temperature. This means that if a compound has adequate solubility in a hot solvent, it can often be recrystallised almost completely by cooling to a temperature at which the solution is supersaturated, *i.e.*, the solubility limit is exceeded.

	DECREASING POLARITY (APPROXIMATE)	
most polar	H ₂ O	water
	RCOOH	organic acids (acetic acid)
	RCONH ₂	amides (N,N-dimethylformamide)
	ROH	alcohols (methanol, ethanol)
	RNH ₂	amines (triethylamine, pyridine)
	RCOR	aldehydes, ketones (acetone)
	RCOOR	esters (ethyl acetate)
	RX	halides (CHCl ₃ >CH ₂ Cl ₂ >CCl ₄)
	ROR	ethers (diethyl ether)
	ArH	aromatics (benzene, toluene)
least polar	RH	alkanes (hexane, petroleum ether)

The solubility of crystalline organic compounds depends on the functional groups that are present and the polarity of the solvent to a very large extent. In this context the expression "like dissolves like" is a very useful principle. Compounds with groups such as -OH, -NH-, -CONH- and others are usually more soluble in solvents such as alcohols or water than in hydrocarbons.

In contrast, non-polar molecules possessing very few or no polar groups will dissolve in hydrocarbons. Regardless of the type of compound, however, the more stable the crystal lattice (the higher the melting point), the less soluble the compound. An example of this is afforded by the isomeric nitrobenzoic acids.

				
		ortho	meta	para
Melting point		147°	141°	242°
Solubility (g/100 ml)	Ethanol	28	33	2.2
	Ether	21	25	0.9

One essential characteristic of a useful solvent is that the desired compound must be considerably more soluble in the solvent when it is hot than when it is cold. To determine whether or not the solvent fulfils this requirement, place a spatula tip (~25 mg) of sample into a small test tube, add a few drops of solvent, and, if the substance does not dissolve in the cold solvent (which would render that particular solvent unsuitable), heat the mixture to boiling point on a steam bath or a water bath. If the material does not go into solution at this point, more solvent may be added, a little at a time with continued heating, until it does. This ensures that the minimum volume of hot solvent has been used to dissolve the sample. The solution is then cooled by placing the tube in a beaker of cold water to see whether the compound will crystallise out.

You should keep in mind the possibility that the compound may dissolve only slowly in the boiling solvent, and also that insoluble impurities may be present in your sample.

b. General Procedures for Recrystallisation**i) Preparing a saturated solution**

Never heat organic solvents or solutions with a Bunsen burner. Use a hot plate or a hot water bath on a hot plate.

The aim is to get the sample dissolved in the minimum volume of hot solvent (that means *just enough hot solvent to get the sample into solution*). Place the impure sample in suitable glassware (test tubes, beakers, flasks – the choice depends on scale *i.e.* how much sample needs to be recrystallised and how much solvent is needed). Place sufficient solvent in an Erlenmeyer flask then heat it on a hot plate. Once the solvent is hot, carefully add hot solvent to the impure sample and stir and/or swirl the sample to try to get it to dissolve. Reheat the solution on the hot plate if needed. Gradually add more hot solvent if needed until all the sample has just dissolved (you need to be careful not to add too much, remember, you are trying to use the minimum volume). Note that if there is an insoluble impurity, you don't have to get it to dissolve but you should filter or decant to remove the impurity (hot filtration might be required).

ii) Decolourisation and hot filtration

Coloured impurities may be removed by using activated charcoal (also known as Norit). This process is carried out by adding activated charcoal to the **cool** solution, then heating to just below boiling. High molecular weight impurities, which often are responsible for dark colour, are selectively adsorbed onto the carbon particles which are then removed via a subsequent hot filtration.

When a crude sample is dissolved in a hot solvent, any insoluble impurities that remain can be removed by filtering the hot solution through a filter paper or through a wad of cotton. This step must be carried out rapidly to prevent the solution from cooling significantly - see the appropriate section for more details.

iii) Crystallisation

When the saturated solution is cooled (or, if necessary, further concentrated by evaporation and cooled, or diluted with a miscible solvent in which the desired compound is less soluble), crystals should start to grow. If crystals do not form spontaneously they may be induced to form by scratching the inside wall of the flask with a glass stirring rod just below the surface of the solvent. The size of the crystals depends on the rate of formation and the number of particles present; shaking the solution speeds up the process and gives smaller crystals.

Just prior to the cold filtration process the flask should be immersed in an ice bath for final cooling. Care should be taken with benzene (mp 5°), glacial acetic acid (mp 17°) and dioxane (mp 11°) that the solvent is not frozen out and a filtration of these crystals attempted.

iv) **Cold filtration under vacuum**

The crystals are collected by swirling and then pouring the mixture of the solid and liquid quickly into a suction filtration apparatus - see the vacuum [filtration techniques](#) for more details.