Recrystallization

A compound formed in a chemical reaction or extracted from some natural source is **rarely pure**.
Recrystallization of solids is a laboratory technique used to purify solids based on their different solubilities.
Other techniques for purifying solids include **sublimation**, **extraction** and **chromatography.**

Solution recrystallization involves dissolving the impure solid in the appropriate solvent at an elevated temperature and allowing the crystals to re-form on cooling, so that any impurity remain in solution.
Solution crystallization takes advantage that almost all solids are ***more*** soluble in a ***hot*** than in a ***cold*** solvent.

The impurity either remains dissolved or removed before cooling by absorption on decolorizing carbon (Norit).
The impurities might not dissolve at all in the hot solution and therefore should be removed by filtration *before* the solution is cooled.

Vacuum(suction) filtration is used to isolate the crystals.

The technique of solution recrystallization involves the following steps:

1. **Selection** of an appropriate solvent.

2. **Dissolution** of the solid to be purified in the solvent near or at its boiling point.

3. **DE coloration** with an activated form of carbon, if necessary, to remove colored impurities and **filtration** of the hot solution to remove insoluble impurities and the decolorizing carbon.

4. **Formation** of crystalline solid from the solution as it cools.

5. **Isolation** of the purified solid by filtration.

6. **Drying** the crystals.

Selection of the solvent

a. The desired compound should be reasonably soluble in the *hot* solvent, about 1 g/20mL, and **insoluble** or *nearly* insoluble in the *cold* solvent. Often the reference temperature for determination of the solubility in “cold” solvent is taken to be room temperature.

b. The impurities should either be **insoluble in the solvent at all temperatures** *or* must remain at least moderately soluble in the cold solvent.

c. The boiling point of the solvent should be low enough so that it can be readily removed from the crystals.

d. The boiling point of the solvent should generally be lower than the melting point of the solid being purified.

e. The solvent should not react chemically with the substance being purified.

f. The solvent should be safe and easy to handle (nonflammable and nontoxic)

g. It should be inexpensive

Selecting a solvent

If the compound has *not* been prepared before, it is necessary to **resort to trial-and-error** techniques to find an appropriate solvent for recrystallization.

- Carry out solubility tests on the compound to be re-crystallized
- Place 0.1 g of the powdered solid into a clean test tube.
- Add the solvent dropwise with shaking.

- **If the solid dissolves, the solvent is not good for crystallization**.

- If it does not dissolve, warm the solution gently to boiling. If it partially dissolves, add more solvent and warm.

- Cool the solution and observe the appearance of crystals.

Note: if the solid does not dissolve in a large amount of the hot solvent, then it is not fit for re-crystallization, in this case try solubility test with a different solvent.

Dissolution of the solid to be purified in the solvent near or at its boiling point.

- Add enough boiling water and few small boiling chips , (Water is the best recrystallization solvent for acetanilide, minimum amount of the solvent should be added for complete dissolution of the precipitate).
- Make gradual addition of water with direct heating on a hot plate or over a wire gauze using Bunsen burner as a heating source. .
- Complete dissolution should be observed with addition of minimum amount of solvent.

DE coloration

- After dissolution of the solid mixture, the solution may be colored.
- If the compound is colored, contaminants may alter the color of the solution.
- If there are colored impurities, the solution is cooled.
- Charcoal (2-3%) of the weight of sample is added to the cold solution which is then boiled with stirring and suction filtered. You should avoid using too much decolorizing carbon because the desired product itself may be adsorbed by it, so less product will be recovered
- The DE coloration step is unnecessary if the solution is colorless.

Formation of crystalline solid from the solution as it cools

- **The hot solution** of solute is allowed to **cool slowly** to room temperature, and crystallization should occur.

- **Rapid cooling** by immersing the flask in water or an ice-water bath tends to lead to the formation of **very small crystals** that may adsorb impurities from solution.

- The formation of crystals larger than about 2 mm should also be avoided because some of the solution may become **occluded or trapped *within*** the crystals. The drying of such crystals is more difficult, and impurities may be left in them.(Gentle agitation of the solution normally induces production of smaller crystals)

- Failure of crystallization to occur after the solution has cooled ,means that either **(diluted solution)** or that the solution is **supersaturated.**
- **A supersaturated** solution can usually be made to produce crystals by ***seeding***.
- **A diluted solution** may be boiled to reduce the total volume then cooled again. (**Concentrate the solution**)

Filtration and Solvent Removal

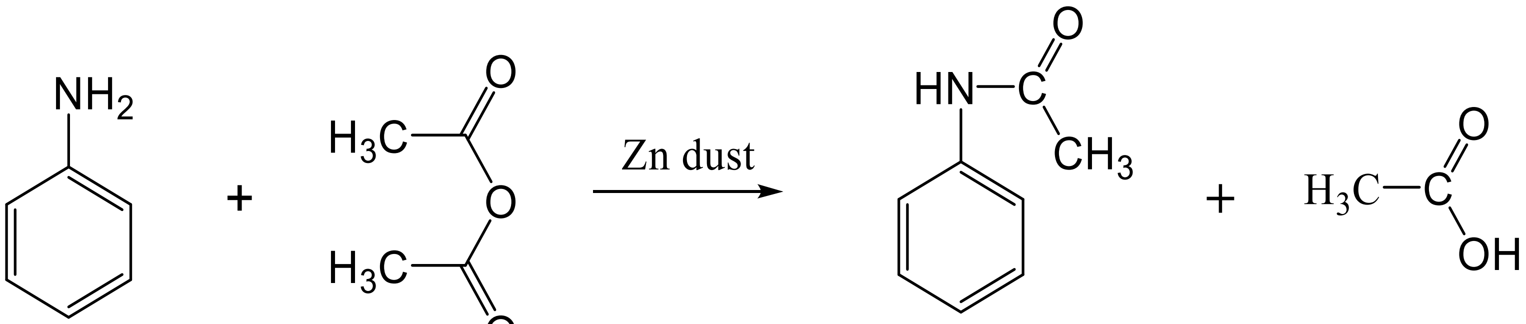
- The crystalline product is isolated by filtration.
- The technique for doing this varies depending on the scale on which the crystallization was performed.
- Suction filtration is preferred at this stage using a Buchner funnel, depending on the scale performed.

Drying the Crystals

- The final traces of solvent are removed by transferring the crystals from the filter paper of the Buchner to a watch glass , a clean paper boat or weighing paper.
- Leave crystals overnight for drying.
- Weight your solid sample and record its melting point before submission to your instructor.

Preparation and Re-crystallization of Acetanilide

Acetanilide is a white solid that can be prepared by reacting aniline and acetic anhydride:



Aniline Acetic anhydride Acetanilide Acetic acid

Basic Information:

Compound	Molecular Mass	M.P. /(B.P.)	Density
Acetanilide	135.17	114 ºC	--------
Aniline	93.13	(184 ºC)	1.022 g/mL
Acetic Anhydride	102.09	(138 ºC)	1.082 g/mL

Experimental Procedure

1. Use a 5-ml dispenser to transfer 5 ml of aniline into a 250 ml Erlenmeyer flask.

2. Add 30 ml of water to the flask.

3. Add a pinch of zinc dust.

4. Add 5 ml of acetic anhydride(using dispenser) in small portions while shaking. Continue shaking until crystals start forming.

5. The product obtained can directly be crystallized in the same flask.
Heat to boiling, then add enough boiling water gradually for complete dissolution of precipitate.

6. Cool a bit and add 0.2 g of decolorizing carbon (Charcoal). The black material (charcoal) will not dissolve.

7. Suction filter out charcoal using a preheated Buchner funnel, then decant the hot filtrate directly(heating the flask and filtrate might be necessary)into a 200 mL clean beaker.

Experimental Procedure: Continued

8. Cool the filtrate to room temperature(less than 40 °C) then in ice-bath. Crystals should appear.

9. Use suction filtration to collect the crystals on a Buchner funnel. Wash the crystals with a small amount of cold water.

10. Keep the suction on to squeeze out all the solvent.

11. Allow your sample to dry overnight, *ask your instructor to lead you for a safe storage place*, **but do not store it in you locker.**

12. Weigh the dry product, calculate the percentage yield and determine its melting point.

13. Collect the product in a paper and write your name and submit it to your instructor.