

Crystallization is used to purify a solid. The process requires a suitable solvent. A suitable solvent is one which readily dissolves the solid (solute) when the solvent is hot but not when it is cold. The best solvents exhibit a large difference in solubility over a reasonable range of temperatures. (eg, Water can be a crystallization solvent between 0-100°C; hydrocarbon solvents such as hexanes or petroleum ether have a different T range since they can be cooled below 0 degrees but boil below 100 degrees).

Characteristics of a solvent:

- chosen for solubilizing power-- solubility usually increases with increasing T
- polarity is important--like dissolves like; polar compounds are more soluble in polar solvents; nonpolar compounds in nonpolar solvents
- should be INERT but few are; eg, acetic acid is sometimes used as a solvent although it will certainly react with basic compounds
- almost all solvents are COMBUSTABLE--avoid flames
- mixed solvents (eg; 1:1 water/methanol) provide a huge range of possible solvents but they must be soluble in one another

Q: Is 95% ethanol a mixed solvent?

Use solvent to get solids into solution but to get them out of solution:

- lower the temperature--solute will be less soluble
- concentrate the solution by removing solvent with a hot plate, heating mantle (flasks), steam bath (use in hood) or with the Roto-Evaporator.

To remove solvent:

- You must have ebullition to concentrate at atmospheric pressure--use a boiling stone, a capillary tube, or agitation.
- If you used reduced pressure to concentrate solution, use the water aspirator with a TRAP in the line. DO NOT turn off the water until the pressure is released. In general, CLAMP any flask that could conceivably trip over.
- Do NOT use ebullition if using the Roto-Evaporator. The rotation provides sufficient agitation.

Crystallization (review)

Used to obtain pure crystalline solid

Use the proper solvent or solvents--test if necessary; a proper solvent will exhibit a big solubility difference over a small temperature range.

Recrystallization or crystallization

- use an Erlenmeyer flask, it is specifically designed for this purpose
- dissolve solid in minimum amount of boiling solvent - add solvent in small amounts. For example, if you add 5 mL and approx. half of the solid dissolves, it should take only another 5 mL to dissolve the remaining half. If some of the solid does not dissolve

then....

c. are remaining particles your compound or insoluble material (eg, sand, old boiling stones)?

d. to determine this, add ca. 10% more hot solvent. If insoluble material, you can decant (carefully transfer solution into another flask leaving the insoluble material behind) or filter.

e. if filtering is necessary, do so to remove suspended solids, the faster the better, keep solution warm so crystallization does not occur (this may require filtering on a hot plate or other heating device).

f. to “decolorize”, use a small amount of charcoal and filter with “filter aid” (see below). For both (e) and (f), rinse filter paper with a small amount of hot solvent.

g. let the filtered liquid (filtrate) cool to room temperature slowly in the Erlenmeyer flask

h. cool the filtrate in an ice-water bath

i. if crystals have not formed

1. “seed” with a small crystal of product, or

2. scratch the flask with a glass rod which has not been fire polished at the end (ask for a demonstration), or

3. add a second solvent dropwise until the “cloud point” is reached; the cloudiness suggests that the solute has reached a saturation point in this new mixed solvent and will start to come out of solution.

j. if material “oils out”, you must redissolve by heating the solution and then proceed again from part (g)

k. if material precipitates out, it is time to filter.

Decolorization:

Most organic compounds are colorless. Highly conjugated compounds (eg, polar polymers) will absorb light in the visible region of the spectrum and thus be “colored”. If these highly polar, large molecules are impurities, they can be removed by use of finely granulated activated charcoal (Norit). Polar compounds (eg, polar impurities) adsorb to the charcoal which is insoluble in the solvent and can be filtered away from solution. Unfortunately, some of your compound will also adsorb if there is enough charcoal so the trick is to use just the right amount. Usually, a very small amount of charcoal will suffice (there is a lot of surface to these particles). The Norit is added in small amounts to the hot (but not boiling) solution until sufficient decolorization has occurred. CAUTION--trapped air in the Norit can cause rapid frothing when it hits the hot solution. The Norit can be filtered from the hot solution using fine filter paper or a **filter aid (Celite)** which is spread on top of the filter paper. To do this, make a slurry of the Celite in any solvent. Wet the filter paper and apply suction to make it stick. Now carefully pour the Celite slurry onto the filter paper so it evenly covers it. Then apply the suction. You may discard the solvent from the filter flask or change filter flasks prior to filtering the Norit containing solution.

Filtering

Used to remove insoluble solids suspended in solution.

Use a GRAVITY FILTER FUNNEL when you DON'T want the solid
Use a HIRSCH or BUCHNER funnel with vacuum when you do want the solid but....
Never use a Hirsch or Buchner funnel with a hot solution unless suggested by your instructor.

For the Hirsch and Buchner funnels, use a piece of round filter paper which fits the funnel. A proper fit is a piece of paper that just covers the holes but does not touch the sides of the funnel (ask for a demo). You will need to use reduced pressure, usually via a water aspirator (be certain that the TRAP is clean). For aqueous solutions, you can use the house vacuum line (be certain that the TRAP is clean).
Just prior to pouring the precipitate onto the filter paper, wet the filter paper with a few mL of solvent and apply the vacuum. This will cause the filter paper to "stick" to the filter.

For the gravity funnel, you can prepare a suitable filter from round filter paper by folding into quarters or by folding it into more than quarters (fluted like a fan). Ask for a demo.
Another trick is to use a piece of cotton or glass wool loosely wedged into the cone of the funnel. It must be tight enough to not move and to trap the solid particles but loose enough to allow the solution to flow through. This procedure is often used to remove drying agents from the solution.

Receiver Flasks: For gravity filtration, you can collect the filtrate in any receiver, including the concentration flask you plan to use immediately thereafter. Be certain to secure the receiver since it will contain your important compound.
For a Hirsch or Buchner funnel, you will need a filter flask with a sidearm for a rubber tubing connection to the TRAP and the reduced pressure source. Use an appropriately sized filter flask, one that will not fill more than halfway and secure this flask so that it does not tip over with that expensive funnel containing your valuable crystals.

TRAP: For suction filtration, you want a clean glass trap in between your filter flask and the suction source. One reason is obvious--in the event that your filtrate is sucked out of the filter flask, it can be trapped and recovered before it goes down the drain or into the house vacuum line. Another reason is that a changing flow of water affects the pressure in the water aspirator so that water can back up and flow towards your filter flask. This way, the trap will fill first and prevent dilution of your filtrate.

Rinsing: You should rinse the gravity funnel with a small amount of solvent to wash down the remaining solution that adheres to the filter paper and funnel. Remember, you want the solution, you do not want the solid. Use a small amount of solvent to prevent excess dilution of the filtrate.

You should rinse the crystals in the Buchner and Hirsch funnel with a minimum amount of cold solvent. Remember, you want the crystals and do not want to dissolve the crystals with excess solvent which will wash them into the filtrate.

The proper way to wash the crystals is to SHUT OFF the vacuum, add a minimum amount of cold solvent so that the crystals are barely sitting in solvent for about 5

seconds (the solvent will not drip through quickly) and then apply the vacuum. The solvent will be sucked into the filtrate. Do this one or two times for each solid. You can air dry the solid by sucking air through the solids. To more rapidly dry a large amount of solid, press another piece of filter paper on top of the solid.

Filtrate from Buchner and Hirsch filtration: The filtrate will probably still contain some of your desired compound and is called the mother liquor. Often, by concentrating this solution further and cooling the solution, one obtains more crystals. This may happen while you are drying the original crystals under reduced pressure. To collect this second batch of crystals, filter as before but do not combine with the first batch of crystals. The purity of this second crop may be different from the first batch. Use melting point or other methods (eg, thin layer chromatography) to determine whether the purity of the second crop is equal to that of the first. If so, they can be combined. If not, keep them separate.

Solvent Polarity in decreasing order:

water

amides (N,N-dimethylformamide)

alcohols (methanol, ethanol)

ketones (acetone, methyl ethyl ketone)

esters (ethyl acetate)

chlorocarbons (methylene chloride, chloroform)

ethers (diethyl ether)

aromatics (toluene)

alkanes (hexanes, petroleum ether)

Heating:

There are different methods used for heating material in the laboratory. Flames are never used in the laboratory except in controlled situations (eg, isolated in fume hoods). Electric hot plates and heating mantles are most commonly used. Be careful not to turn this equipment to its highest setting which can burn it out. It does take several minutes for these instruments to reach the desired temperature. The heating mantles are plugged into a variable rheostat which provides a temperature control. Heating mantles are used for round-bottom flasks (rbf); choose an appropriate size to fit the flask you plan to use.

Steam is often used for heating volatile, non-aqueous, flammable solvents in the fume hoods. This is preferable to using hot plates which can lead to flash fires. The 100°C maximum temperature from steam is sufficient for most commonly used organic solvents including many mixed aqueous solvents.

Steam bath vs hot plate:

Advantages: can only heat to 100°C so cannot overheat the compounds in solution;
flash fires are unlikely with most solvents
provides instant heat

Disadvantages: can only heat to 100°C so may not be suitable for higher boiling solvents;

steam condenses to water which can get into your flask
steam line is not as portable as a hot plate
temperature control is more difficult

Melting Point Determination:

The standard physical property of a solid is its melting point. The melting point is actually a melting point range. It is used to help determine the purity of a solid and to help verify the identity of the compound. A pure compound should melt over a narrow temperature range. Impurities usually cause the melting point range to widen and lower in value. To obtain the melting point range, you record the temperature at which the first crystals begin to melt (solid to liquid phase) and the temperature at which the last crystal melts, eg; m.p. 124-126°C. Important considerations include: 1. do you have a representative sample of your compound or have you fished out the best looking crystal for a melting point; and 2. is the thermometer you are using correctly calibrated. If not, you will obtain incorrect values.

There are several different mp apparatus in the laboratory. The most common is a Fisher-Johns apparatus whereby the crystalline sample is sandwiched between two glass discs and placed on a small hot plate. The temperature of the hot plate can be adjusted using the rheostat on the instrument. Temperatures respond fairly quickly to settings of the rheostat and can be read from the thermometer inserted into the hot plate. You assume in using this apparatus that the temperature of the crystals is equal to the temperature of the hot plate as measured by the thermometer. This is only correct if the rate of heating is low, 1-3 degrees/minute. You may assume that the thermometers read correctly although this can be tested and calibrated by determining the mp of "standard" compounds.

Preparing your sample for the Fisher-Johns apparatus: Take a small amount of your crystalline material (less than 1 mg!) and place it on a glass disc. Cover with another glass disc and carefully crush the two together, rotating one disc over the other to produce a finely ground material. Place this sandwich on the hot plate and heat rapidly (10-20 degrees/min) until the material melts. This will give you a rapid, but inaccurate reading. Now cool the hot plate down to about 20 degrees below the observed inaccurate mp and repeat the experiment. Increase the temperature until you are 10-15 degrees below the expected mp at which time lower the rate of heating to 1-2 degrees/minute. Common errors: rate of heating is too rapid (results in a higher mp); amount of material is too large (will increase your mp range); crystals are not ground flat (results in a higher mp and broad mp range since an air gap is present which helps to cool the crystals); crystals are not dry. To rapidly dry a few wet crystals, place them onto a small piece of filter paper, rub them onto the paper with a clean spatula until all of the liquid is drawn into the paper. Carefully scrape the crystals away from the paper.

The Mel-Temp apparatus and Thomas-Hoover apparatus: The dry, crystalline sample is placed in an open ended capillary tube which will be heated by air or by oil. One advantage over a Fisher-Johns apparatus is that 3-5 samples can be observed at the same time allowing you to take the melting point of many samples simultaneously. Also, it is possible to take the mp of a sample that sublimes prior to its mp (one uses a

sealed capillary). Once again, a rheostat is used to control the heating rate. Ask for a demonstration.

Preparing the sample in a capillary tube: The sample must be dry or else you cannot get it into the capillary tube. The capillary tube should be open at one end only. Tamp the open end onto your crystals until a few collect inside the mouth of the capillary. Now tap the crystals to the closed bottom end by vibration (there is a vibrator on the Thomas-Hoover apparatus) and/or by bouncing the capillary (bottom end down) through the open space of a large piece of glass tubing. Ask for a demo. Follow the instructions given above for the rate of heating.

Extraction

Extraction is a method for moving a compound from one medium to another. For example, if you make coffee from coffee beans, you are extracting some flavorful components of the bean and some caffeine into the water. The remainder of the beans (grounds) are left behind and discarded. This is called a solid-liquid extraction. If you are trying to move a compound from one liquid phase (solvent 1) into another liquid phase (solvent 2), this is liquid-liquid extraction but the two solvents must be immiscible or insoluble to the extent that they form two distinct layers (why?). The compound is now distributed into two solvent layers which can be separated. By measuring the concentrations of compound in the two solvents (c_1 and c_2) we obtain a distribution coefficient, K , which is a constant for a given compound and given solvents *at a given temperature*, irrespective of the amounts of solvent present. A simple equation shows the relationship $K=c_2/c_1$.

Liquid-liquid extractions are common in organic chemistry. Usually, one of the solvents is water and the objective is to remove a component from an aqueous solution into a solvent such as ether, methylene chloride, or hexane (all of which have low water solubility). Often, water-insoluble organic solvents, such as ether, methylene chloride and hexane, may contain some undesirable water soluble components (like HCl). In that case, we would extract those components out of the organic solvent by using water as the second solvent. That is often called a water wash. You will have an opportunity to do several extractions and water washes. For these purposes, you will use a separatory funnel.

The rule of thumb for liquid-liquid extractions is that several small extractions are more efficient than one big extraction. Test this out as follows:

If $K=6.0$, then $c_2/c_1=6.0$ or $(g/mL_2)/(g/mL_1)=6$. If you have 2.0 g in 200 mL of water and want to extract with a total of 100 mL of solvent 2, let us determine if it is better to use one extraction with 100 mL or two 50 mL extractions.

The distribution in the former case is $(x/100 \text{ mL})/(2.0-x/200 \text{ mL})=6.0$ where x is grams in solvent 2 and $2-x$ is grams in water. Solving for x , gives us $x=1.5$ g, leaving 0.5 g in the water.

In the latter case, we have $(x/50 \text{ mL})/(2.0-x/200 \text{ mL})=6.0$; solving for x gives us $x=1.2$ g leaving 0.8 g in the water for the first extraction. The second extraction is $(x/50 \text{ mL})/(0.8-x/200 \text{ mL})=6.0$; solving for $x=0.48$; which means that in the two 50 mL extractions we obtained $1.2 + 0.48 = 1.68$ g, leaving 0.32 g in the water. The two

extractions were clearly more efficient than one extraction. Four 25 mL extractions would have been even better but there are practical limits.

Separatory Funnel: This glass equipment is very cleverly designed to carry out the task of separating two immiscible liquids (which form two distinct layers). Work with this equipment in a proper fashion and it will perform remarkably well. However, read the instructions first and follow the steps carefully.

Use of the Separatory funnel: First, check that the stopper fits and that the stopcock works properly. Glass stopcocks must be greased; Teflon stopcocks do not need grease.

2. Close the stopcock and support the funnel using a ring clamp.
3. Place a beaker underneath the funnel to catch any spills or leaks.
4. Fill the funnel with the two solvents. Do not fill the funnel more than 75% of capacity (so plan ahead in choosing the proper size funnel)
5. Stopper. Remove the funnel from the stand, hold properly and invert (IMPORTANT, ask for a demo), release any pressure buildup by opening the stopcock repeatedly BEFORE shaking (and then after shaking).
6. After returning the funnel to the stand where it is secured, loosen the stopper immediately--shaking builds up pressure
7. When the two phases separate, draw off the lower layer.
8. Pour out the upper layer if necessary. NOTE: The funnel is designed to retain the last few drops.
9. Save both upper and lower layers until you are *certain* that you have the compound you want. If you do not throw it away, it is not lost. I repeat, **never** throw away a layer unless you are certain that you will never need it.

Percent Theoretical Yield: Although you may have obtained the product you desired, the amount of material you obtained (in grams), compared to the amount you could have obtained (in grams), is a valuable piece of information. It can suggest that you did or did not run the reaction efficiently or that other products may have been formed via other reactions. To calculate % Theoretical Yield you must first calculate the theoretical yield. You then take $actual\ yield/theoretical\ yield \times 100 = \% \text{ theoretical yield}$.

The % theoretical yield can never exceed 100%; if it does, it may mean that your sample is wet or contains extraneous material, such as a boiling stone.

Labels

Properly label your sample vials when you submit your products for grading.

BENZOIC ACID (*appropriate, unambiguous name of the compound*)

mp 120-121°C (*melting point observed for this sample*)

3.2 g (*amount in vial*)

D.L. Green (*the name of the person submitting the sample*)

1/15/96 (*date submitted*)

(DLG 12-14 *which is a reference to notebook pages concerning this material*).

Properly label your spectra. The infrared spectra you decide to save should be labelled immediately. List the name of the compound or some identifying term if the name is unknown, your name, and the method by which the spectrum was obtained. The instrument will automatically print the date but, if it doesn't, be certain that you list the date it was recorded on the spectrum.