

Experiment 2

RECRYSTALLIZATION: PURIFICATION OF SOLIDS

Fig. 2-1



Louis Pasteur (1822 - 1895). Developed germ theory of disease. Separated enantiomers using recrystallization (1848)
http://ambafrance-ca.org/HYPERLAB/PEOPLE/_pasteur.html

New Techniques, Comments

Recrystallization, vacuum filtration.

Discussion and Techniques

Your adventure in organic chemistry continues with one of the most important separation and purification techniques appropriately called recrystallization. Whether a compound is obtained from a synthesis, extraction from a natural product or even a stockroom bottle, it is often necessary to increase the purity of the substance. The most commonly used technique for the separation and purification of solids is called recrystallization. This technique utilizes the observation that the solubility of most solids in liquids increases dramatically as the solvent temperature is increased. Most solutes that are exceptions to this generalization are ionic compounds.

For the procedure of recrystallization, a barely saturated solution of the solid in the hot (commonly at the boiling point) solvent is prepared and allowed to cool. The solubility decreases as the temperature drops. Solid crystallizes out of the solution and is cooled further in an ice bath and filtered and dried. Insoluble impurities are removed by filtration of the hot saturated solution and soluble impurities dissolve in the solvent and do not crystallize back out upon cooling. These impurities pass through the final cold filtration. Several steps are followed in a typical recrystallization.

- A. Solvent selection - In the ideal solvent, the compound will have very low solubility in cold (~ 0-5°C) solvent and substantial solubility in hot solvent. If the boiling point of the solvent is between 25°C and 50°C, there will not be much of a temperature range available for increasing solubility. This means that some common solvents such as ether (b.p. = 35°C), pentane (b.p. = 35°C) and methylene chloride (b.p. = 40°C) should only be used for recrystallization when better alternatives cannot be found.

Very high boiling solvents are sometimes not desirable. After recrystallization, it is often necessary to wait for the residual solvent to evaporate. For example, when water is used as a solvent, it is often necessary to wait several days for sufficient drying to be achieved. Unlike your experience with inorganic compounds in general chemistry, oven drying is usually not an option as organic compounds tend to decompose at elevated temperatures. Also, during the recrystallization procedure, it is sometimes necessary to evaporate or concentrate the solvent and for this and safety reasons, a very high boiling point is not convenient. Thus a temperature range of 50°C to about 80°C is preferable for the solvent boiling point. It is also best if the solvent has a boiling point below the melting point of the compound. This helps to avoid undesirable oiling out (discussed later). Low toxicity and cost are two more criteria to consider.

The first step in recrystallization is to perform qualitative test tube scale tests to find an appropriate solvent. An abbreviated list of possible solvents arranged according to approximate increasing polarity is included in *Table 1-1* below. A more extensive list is available in *Appendix B*. Usually, a small amount of the compound is put in a test tube or in several tubes if several solvents are going to be tested simultaneously. The solid is covered with a small amount of solvent. If the solid dissolves, the solvent is not useful by itself as a recrystallization solvent but the solubility observations should be noted in your lab book. If little or none of the solid appears to dissolve, a boiling stick is added to minimize bumping and the test tube is held with a test tube clamp in a boiling water bath. If the solid still has not dissolved when the solvent boils, more solvent is added slowly with a Beral or disposable pipet while maintaining boiling. If the addition of more solvent causes more solid to dissolve, continue to add solvent until all of the solid has dissolved. If the solid does not dissolve at the boiling point even after substantial solvent has been added, the solvent will not be useful alone but your solubility observations should be noted in your lab book. If addition of solvent to the boiling solution does result in the solid dissolving, the solvent should be suitable for use in recrystallization of the compound. However, it is wise to let the test tube cool and then immerse it in an ice bath. If recrystallization does not occur, scratch the inside of the test tube with a glass rod. If recrystallization still does not occur, the dependence of solubility on temperature should be rechecked or another solvent used.

Experience does help with solvent selection. Hopefully, you gained some insight into solvents and their properties in *Experiment 1*. For very polar compounds, it is unlikely that non-polar solvents such as hexane will work. And vice versa, for non-polar compounds, very polar solvents such as water are probably not going to work. It is also possible that solids will be too soluble in solvents that have about the same polarity as the solid. If you have no idea which solvent to start with, start with a non-polar solvent and increase the solvent polarity until you find one that works. *Table 2-1* does include relative polarities. For a more extensive table of solvent properties, see *Appendix B*.

Table 2-1

<u>Solvent</u>	<u>formula</u>	<u>boil.</u> <u>pt.</u> <u>(°C)</u>	<u>melt.</u> <u>pt.</u> <u>(°C)</u>	<u>density</u> <u>(g/mL)</u>	<u>H₂O</u> <u>sol.</u> <u>(%)</u>	<u>relative</u> <u>polarity</u>	<u>LD₅₀</u> <u>(oral-rat)</u> <u>(g/kg)</u>	<u>flash</u> <u>pt.</u> <u>(°C)</u>
cyclohexane	C ₆ H ₁₂	80.7	6.6	0.779	<0.1	0.006	13	-20
hexane	C ₆ H ₁₄	69	-95	0.655	0.014	0.009	29	-23
toluene	C ₇ H ₈	110.6	-93	0.867	0.05	0.099	5	4
ethyl acetate	C ₄ H ₈ O ₂	77	-83.6	0.894	8.7	0.228	11	-4
chloroform	CHCl ₃	61.2	-63.5	1.498	0.8	0.259	1.2	
2-butanone	C ₄ H ₈ O	79.6	-86.3	0.805	25.6	0.327	2.7	-7
acetone	C ₃ H ₆ O	56.2	-94.3	0.786	M	0.355	9.8	-18
2-propanol	C ₃ H ₈ O	82.4	-88.5	0.785	M	0.546	5.0	12
ethanol	C ₂ H ₆ O	78.5	-114.1	0.789	M	0.654	7.1	13
methanol	CH ₄ O	64.6	-98	0.791	M	0.762	5.6	12
water	H ₂ O	100.00	0.00	0.998	M	1.000		

Sometimes, it is not possible to find a common solvent that satisfies the criteria needed. In cases of this type, it may be necessary to resort to a mixed solvent system. First of all, the two solvents to be mixed must be miscible. A mixture of water and hexane will not form a useable mixed solvent for recrystallization. In an earlier paragraph, there were instructions to note in your observations when the solid was either too soluble or insoluble in a solvent. A mixed solvent will consist of a mixture of one of each but with the noted requirement that the two solvents are miscible. There are two ways to approach recrystallization from a mixed solvent.

1. Cover the solid with a small amount of the solvent in which it is insoluble. Heat the system to the boiling point of the solvent and start adding the other solvent while maintaining boiling until the solid dissolves. Remove from the heat source and proceed as indicated in later paragraphs.
2. Add a sufficient amount of the good solvent to dissolve the sample. Heat the mixture to the boiling point of the solvent and start adding the other solvent while maintaining boiling until a slight amount of cloudiness or precipitate appears. Then proceed as indicated in later paragraphs.

The choice between 1 and 2 is best made using a comparison of the boiling point of the two solvents. It is better to start with the lower boiling solvent so that addition of the second solvent does not result in having it immediately boil out. Consider what will happen if the lower boiling solvent is added to the boiling original solvent if the boiling point of the original solvent is the higher of the two.

A few comments about specific solvents are in order. Since most organic compounds have very low solubility in cold and hot water, water usually does not work as a recrystallization solvent. In addition, since water has a lower volatility than commonly used organic solvents, samples recrystallized from water usually take much longer to dry. However, water is often the solvent of choice for some carboxylic acids, phenols and amides.

Several decades ago, solvents such as benzene and carbon tetrachloride were commonly used as recrystallization solvents. However, because of toxicity and carcinogenicity considerations, it is strongly preferable to find alternatives. Toluene is frequently used instead of benzene but its boiling point (111°C) is somewhat high. Chloroform is sometimes used as an alternative to carbon tetrachloride but also is hazardous and is more polar and therefore has different solvent properties.

Hexane and cyclohexane are non-polar hydrocarbon solvents. Sometimes you might note that the bottle has "hexanes" on the label rather than hexane. This means the bottle contains a mixture of isomeric hexanes and probably will work as replacement solvent for hexane and is less expensive. Additionally, you will find hydrocarbon solvents labeled as petroleum ether or ligroin. Usually, a boiling range is also included as these solvents contain mixtures of hydrocarbons with similar boiling points. Again, they can usually be substituted for a single hydrocarbon for recrystallization purposes. **Do note that petroleum ether is not an ether (ethers such as diethyl ether contain two hydrocarbon groups joined by an oxygen R-O-R) but is a mixture of hydrocarbons that do not contain oxygens.**

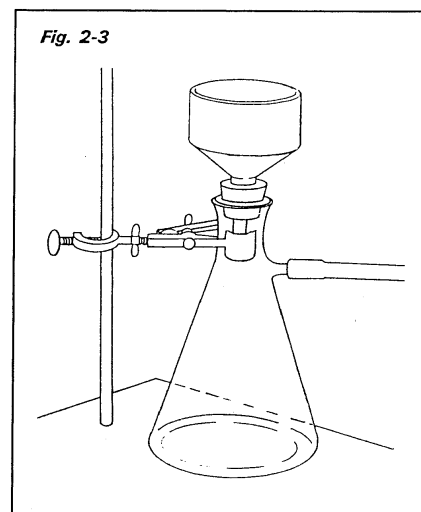
- B. Dissolving of solid - A desired amount of compound to be recrystallized is weighed out usually into an Erlenmeyer flask. Do not recrystallize the entire sample. If a mistake is made such as spilling, you want to make sure you have enough to try again. You also may need a crystal for use as a seed in a later step. The solid is covered with the chosen solvent, a boiling stick inserted and the mixture heated to the boiling point on a hot plate. After boiling is achieved, solvent is added with a Beral pipet while boiling is maintained until the solid dissolves. If an impurity is present that does not dissolve, then a hot filtration should be performed as described in C below. If the sample totally dissolves, the mixture is removed from the heat source and step C can be skipped. Note the special instructions above if a mixed solvent is used.
- C. Decolorizing - If the compound is known to be white (white is by far the most common color for solids) and a colored solution results from dissolving the compound, some chemists suggest that an attempt should be made to decolorize the solution using decolorizing carbon also known as norit. If you choose to use this technique, allow the colored solution to cool to near room temperature and add about a pinch of the decolorizing carbon to the solution and reheat to boiling. Because an insoluble impurity (the carbon is now present) a hot filtration needs to be performed. Decolorizing should only be performed if absolutely necessary as it usually results in substantial loss of product.

- D. Hot filtration - If an undissolved solid remains in the boiling solvent, a hot filtration is necessary. However, do not use this technique unless it is needed as it usually results in some loss of your compound. Since decolorizing creates this situation, it should be avoided unless needed. The problem is that as the hot solution is filtered, it cools and the temperature drops below the saturation point causing crystallization to occur on the filter paper and in the funnel. To help minimize this effect, extra solvent should be used. This causes a loss as the compound is at least slightly soluble in the cold solvent but this loss is usually less than the loss caused by crystallization on the funnel and paper. To avoid a loss from the increased solubility, the solvent can be partially evaporated after the hot filtration. A hot filtration also suffers from the additional disadvantage that it should be a gravity filtration rather than a vacuum filtration (why?). To increase the speed of the filtration somewhat, it is best to use fluted filter paper rather than the traditional quarter folded filter paper (why should it filter faster with fluted paper). It also helps if the procedure is carried out with the flask and filter on top of a steam bath. The steam helps to keep the funnel warm and hopefully minimizes crystallization. Filter the hot solution in small amounts returning the mixture to the heat source before each transfer to keep the solution as hot as possible during filtration.
- E. Solution cooling - Depending on time considerations, the solution is allowed to cool on the desk top to room temperature. Slow cooling usually yields larger and purer crystals. If time is of the essence, cool the solution in an ice bath.
- F. Oiling Out - Occasionally, product separates out of solution in the liquid phase. This is a very undesirable result as the impurities tend to concentrate in the liquid of the desired compound and the result of the recrystallization is the opposite of what is desired, a decrease in purity. Oiling out most commonly occurs when the melting point of the compound is lower than the boiling point of the solvent. Try to choose a solvent that has a boiling point lower than the melting point of your compound. If this cannot be done, add extra solvent to the boiling solution. This decreases the saturation temperature hopefully below the melting point but does cause a lower yield as more will remain dissolved at low temperature. Sometimes oiling out can be avoided if the solution is cooled quickly in an ice bath.
- G. Crystallization - It is not uncommon for a supersaturated solution without formation of crystals to form as cooling occurs. If this happens, several techniques should be tried to induce crystallization.
1. Cool the mixture further in an ice bath. Normally, you are going to do this anyway before the next step to further decrease the solubility and increase the percent recovery.
 2. While cooling in an ice bath, scratch the inside of the flask with a glass rod. The tiny glass specks that are produced sometimes act as nuclei for condensation of the compound and crystallization then proceeds rapidly.
 3. While cooling in an ice bath, add a seed crystal of the compound.
- H. Ice bath cooling - If you have not already done this to induce crystallization, the solution is usually cooled with an ice bath to further decrease the solubility of the solid in the solvent.
- I. Vacuum filtration - A Büchner funnel, a filter flask, and an aspirator are used to collect the solid. Be sure to transfer as much of the solid as possible from the flask to the Büchner funnel. This may require scraping with a spatula and should include rinsing the flask with a small amount of ice-cold solvent once or twice. The washings should be added to the Büchner funnel. See Figures 2-2 and 2-3.

You have undoubtedly performed a gravity filtration previously that used gravity to pull the liquid through a filter and left the solid on the filter paper. Since gravity filtrations tend to be slow, chemists often use the assistance of a vacuum to increase the rate of filtration. A vacuum filtration most often uses a Büchner funnel (or for very small amounts, a Hirsch funnel) with a fitted piece of filter paper and



Figure 2-2



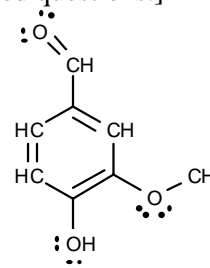
a filter flask connected to a water aspirator. A water aspirator is simply a piece of tubing with narrow hole to a sidearm. The sidearm is connected to the apparatus using vacuum tubing (thick walled that doesn't collapse under vacuum). The water is turned on to full flow and as the water flows by the narrow opening, air is pulled into the water stream. The minimum pressure attainable for a water aspirator is the vapor pressure of the water at the temperature of the water. This means that for water at 20°C, the pressure in the system will be reduced from about 760 mm to 18 mm (assuming no leaks). For more information on how the aspirator works, consult a physicist or look up Bernoulli's Principle. As water pressure changes often result in water backing up in the hoses to the flask, a trap should be included between the aspirator and the filter flask. **The trap is especially important when you are collecting the filtrate rather than the solid.**

- J. Washing the crystals - While the crystals are still in the Büchner funnel, they are usually washed with ice-cold solvent once or twice more. Be sure to minimize the quantity of solvent as the product is slightly soluble in the ice-cold solvent. The aspirator should be left on for a few minutes to pull air through the sample to help dry the sample.
- K. Drying - The crystals are usually allowed to sit until evaporation of the solvent is complete. Depending on the volatility of the solvent, this will probably take several hours and is best done overnight by leaving it protected but not covered in your lab drawer until the next lab day.
- L. Percent recovery - After drying, the mass of the recrystallized sample divided by the mass of the starting solid times 100% is the % recovery.
- M. Purity determination - The purity of the sample is usually determined by a simple physical measurement such as melting point. This procedure needs to be done after drying as solvent remnants act as impurities and depress melting points. To verify identity, it may be necessary to do a mixed melting point or to determine additional properties.

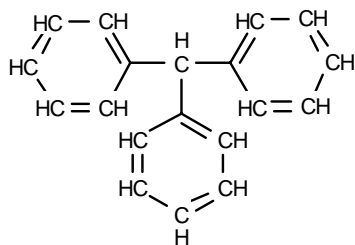
Procedure [For this section of your report, it is not necessary to restate the procedure given but the source of the procedure should be cited. The report should contain explanations of the italicized questions.]

Two recrystallizations, vanillin and an unknown, will be performed.

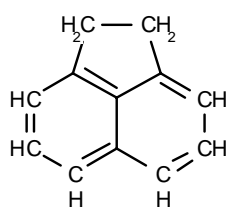
- A. **RECRYSTALLIZATION OF VANILLIN** (4-hydroxy-3-methoxybenzaldehyde). Assume you work for a flavor company and a shipment of vanillin comes in that you suspect is impure. Your task this week is to purify the vanillin by *recrystallization*. Next week you will evaluate the purity of the impure and purified vanillin samples by taking melting points. You will also determine the percent recovery.



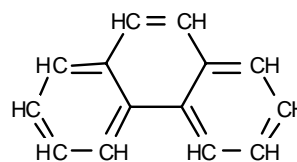
1. Weigh into a 125 mL or 250 mL Erlenmeyer flask about 2 grams of your vanillin and record the amount in your lab reports for *Experiments 2* and *3*.
 2. Add about 60 mL of water to the flask and stir vigorously.
 3. Heat the solution just to the boiling point and stir until all the vanillin dissolves.
 4. Place the flask in an ice bath for 5 minutes and stir occasionally.
 5. Place a properly fitted piece of filter paper in your Büchner funnel. Make certain that all of the holes are covered. Wet the paper thoroughly with deionized water from your wash bottle and vacuum filter your vanillin crystals. Rinse the Erlenmeyer flask once or twice with 5 mL of ice-cooled water and use this water to wash the crystals in the funnel.
 6. Empty the crystals onto a weighed piece of filter paper and place them in your desk for drying, being sure they cannot spill.
- B. **Unknown.** Many students think that one of the most enjoyable challenges in the organic lab is the identification of unknowns. In today's experiment, you will be given about 2 g of one of the following: triphenylmethane, acenaphthene or phenanthrene. Using small amounts in a test tube, test for solubility in cold and hot solvents. After you have selected an appropriate solvent, recrystallize about half (**be sure you record the mass and insert the value in the data table for *Experiment 3***) of the sample from the solvent. The crystals should be saved and allowed to dry for your next lab where you will determine the percent recovery, melting point and identity of the product. Be sure to save some of the original (impure) unknown for a melting range determination next week.



triphenylmethane



acenaphthene



phenanthrene

References

Murov, S.; Stedjee, B. *Experiments and Exercises in Basic Chemistry*, 7th ed., Wiley, **2009**, 55.
Murov, S. *Experiments in General Chemistry*, 5th ed., Brooks/Cole, **2007**, 23.

Prelaboratory Preparation - Experiment 2

At the beginning of your report in your notebook, you should list the goals of this experiment. You should prepare a table that will contain all the pertinent observations. For the unknowns, you should look up the melting points of triphenylmethane, aceaphthene and phenanthrene. Make sure you familiarize yourself with the technique of recrystallization.

Generally, it is not necessary to repeat the procedure in your notebook but the source of the procedure should be cited. However, if the procedure is modified in any way, complete documentation of the nature of the changes and the reasons for the changes is required.

Observations

REPORTING OBSERVATIONS. Be sure to immediately record all observations directly (not on scratch paper) in your notebook. In this experiment, the observations will include all solubility observations and mass measurements as well as descriptions of key changes that occur during the procedures. The measurements should be recorded in the table prepared in the **Prelaboratory Preparation** section. Make sure you make and record observations carefully, completely and without bias. Be sure to record what happens rather than what you expect to happen. Often, observations that you might not consider to be important turn out to be the clues that lead to important discoveries. You can decide later if the observation needs to be considered further. Many examples of serendipitous discoveries that can be attributed to the very alert and careful observations of the discoverer include penicillin, artificial sweeteners and teflon. Ponder the words of Pasteur, Emerson, Churchill and Bokonon:

“In the fields of observation, chance favors only the mind that is prepared.” *Louis Pasteur*

“God hides things by putting them near us.” *Ralph Waldo Emerson*

“Man will occasionally stumble over the truth, but most of the time he will pick himself up and continue on.” *Winston Churchill*

“Where we go matters less than what we notice.” This is part of a poem that is attributed to Bokonon from *The Lost Book*.

Conclusions

This section should include the following:

1. Were the goals of the experiment achieved? Explain your answer.
2. Explain how you selected the recrystallization solvent for your unknown.
3. When is recrystallization an appropriate technique for purification (e.g., is there an ideal sample size range, is there a minimum starting purity, what final purity should be expected, etc.)