TECHNIQUE 5

Crystallization

Alternate Methods for Recrystallization and/or Filtration

In recent years several alternative methods have been reported for the recrystallization and or filtration of small quantities of solid product. Several of these methods are summarized here. Consult the sited references for further details.

a. Landgrebe (see Landgrebe, J.A. J. Chem. Educ. 1988, 65, 460) has described the use of a recrystallization pipet. The method works well for 10-100 mg quantities, as long as the volume of solvent used in the recrystallization does not exceed 1.5 mL, the capacity of a Pasteur pipet. The sequence of steps follows:

1. A recrystallization tube is prepared (Website Fig. 5.12W) by pushing a plug of cotton (copper wire is used) into the Pasteur pipet so that the cotton resides 1-1.5 cm below the wider bore of the pipet.

2. The lower part of the tube is sealed below the cotton plug with a micro burner and the glass is pulled so that a very narrow tip is formed. This allows the tip to be broken easily at a later stage of the operation.
3. The solid to be recrystallized is placed in the tared tube, the tube reweighed to determine the weight of solid, and then it is clamped in a vertical position. A tared vial is placed so that the bottom tip of the recrystallization tube protrudes about 1 cm into it. (Website Fig. 5.13W).

**Website Fig. 5.13W**

Dissolution of sample in hot solvent.

4. An appropriate amount of solvent is added to the tube using a Pasteur pipet, and the suspension stirred with a copper wire. At this point a heating lamp is placed approximately 6-8 cm from the tube.

5. When the solid has dissolved, the vial is removed, the tip snapped off and the vial quickly replaced. If the filtration into the vial is too slow, pressure is applied using a pipet bulb.

6. After crystallization is complete, the mother liquor may be removed using a Pasteur filter pipet. Cold, fresh solvent may be added to wash the crystals, and
the wash solvent again removed as before using the Pasteur filter pipet. The washed crystals may be dried under reduce pressure as discussed earlier.

b. Laporterie (see A. Laporterie J. Chem. Educ. 1992, 69, A42) outlines the construction of an assembly consisting of a reaction tube fitted with a filter paper-glass wool plug supported by a one hole rubber stopper into which a hypodermic syringe needle is inserted. An adapter is inserted through the stopper hole so that the assembly can fit a filtering flask. This simple and inexpensive system allows one to filter, wash and crystallize without transferring the product crystals.

c. Durate and co-workers (see F. F. Duarte; L. L. McCoy; F. D. Popp J. Chem. Educ. 1992, 69, A314) report an apparatus for recrystallization of small amounts of material which is less imposing and/or frustrating, for the average organic laboratory student when compared to the Craig tube or filter Pasteur pipet techniques. The system is also more durable. It consists of a 10 mm x 127 mm glass tube closed on one end by a coarse frit that fits snugly in a 16 mm x 95 mm glass tube. The material to be recrystallized is placed in the outer tube, the solvent of choice is added, and the system heated as in a normal crystallization. The resulting solution is cooled and once the crystals are formed, the inner tube is placed in the outer tube and the apparatus is centrifuged. The mother liquor is forced into the inner tube. The liquor is removed with a Pasteur pipet leaving the purified material in the outer tube. The tubes are separated and the crystals dried.

d. An other alternative approach has been reported by Winkel (see C. R. Winkel J. Chem. Educ. 1993, 70, A161). A 10-mL culture tube with small holes drilled through its Bakelite screw cap is used. Filter paper (1.5 cm) is placed in the cap and secured when the cap is screwed onto the tube. The inverted tube is inserted into a neoprene rubber
connector, made from a #3 neoprene stopper, which in turn is placed in a side arm suction tube. The suction tube holds a collecting tube. The filtrate is directed into the collection tube by a plastic funnel base secured in the neoprene adapter. This assembly has several advantages. Loss of crystals and time in making sample transfers are avoided. Hot and cold filtrations can be done easily. Heat and vacuum can both be applied for fast drying. No suction trap is required to prevent back-splashing, if a spacer is used and no centrifugation is necessary in order to remove the mother liquor.

e. An inexpensive single-use suction microfilter has been described by McDevitt (see E. J. McDevitt J. Chem. Educ. 1994, 71, A147).

The apparatus is prepared from two disposable polyethylene transfer pipets. The top hemispherical portions of the droppers are punctured 4 or more times with a pin. The hemispheres are then cut off each dropper. One of the punctured hemispheres is then inserted into the bulb of a cut dropper and pushed to the bottom with a rod. A small wad of glass wool is then inserted followed by the second punctured hemisphere until it rests on the glass wool. Thus, a sphere-wool-sphere sandwich is constructed at the base of the bulb. This suction filter is used in the usual manner. The collected crystals can be pushed out of the bulb or the dropper-funnel can be cut apart.

f. Filtration may be carried out using a Pasteur pipet, if the volume of solvent does not exceed 3.0 mL of solution (see J. W. Zubrick The Organic Chem Lab Survival Manual 4th ed., Wiley: New York, NY, 1997, p. 82). Push a small plug of cotton into the Pasteur pipet so that the cotton resides slightly into the narrow portion of the pipet and shorten the tip of the pipet to approximately 1.5–2 cm. Do not use too much cotton or pack it too tightly so that the solution cannot be forced through it. The warm solution to be filtered is placed in the pipet using a preheated second Pasteur pipet. The solution is then allowed to filter through the cotton plug into a clean vial (tared if
desired). If need be, pressure can be applied by a pipet bulb (*careful*!). It as advisable to place a heating lamp approximately 6-8 cm from the tube since a serious problem with this technique is that crystallization often occurs in the filtration tube. The shortened Pasteur filter pipet can easily be suspended over a collection vial using a cradel made by twisting two short pieces of copper wire together which are then spread apart to snugly accept the pipet.

**g.** Separation of crystalline solids or of impurities can often be accomplished, with care, by use of a Pasteur *filter* pipet (Website Fig. 5.14a-dW).

**Website Fig. 5.14a-dW**

![Diagram of Pasteur filter pipet preparation](image)

Preparation of Pasteur filter pipet.

The container (conical vial or centrifuge tube) holding the crystal-mother liquor mixture is cooled in an ice-water bath. A Pasteur filter pipet is used to slightly stir the mixture. The air is then *slowly* pushed from the pipet as the tip of the pipet is inserted to
the bottom of the container (the bubbles of air forced from the tip clear a path for the
tip of the pipet so that it can reach the bottom of the flask without trapping crystals in
the tip as it is pressed against the surface of the glass). The liquid is then drawn slowly up
into the pipet leaving the crystals behind. Cold, fresh solvent may be added to wash the
crystals, and the wash solvent then removed using the Pasteur filter pipet as before.

This method is not recommended for fine crystals. Large needles or granular type
materials may be filtered in this manner.

Two Examples to Practice Recrystallization on a semi-microscale are given here. This
procedure is useful when carrying out scaled-up micro scale reactions.

Example [5AW]: Recrystallization of Benzoin.

Place about 250 mg of benzoin in a 25 mL Erlenmeyer flask. Add a boiling stone,
stirring rod or if a magnetic stirring hot plate is used, a small magnetic stir bar. Add
enough preheated 95% ethanol to cover the crystals and then heat on a sand bath.
When the mixture is at a low boil, add dropwise (Pasteur pipet) small amounts of the
solvent just to the point where all the benzoin goes into solution.

We will assume that the solution is colored and that it also has some insoluble impurities
still present.

Cool the solution somewhat and add carefully about 1–5 mg of Norit pellets to
absorb the colored impurities. If powdered charcoal is used be careful during the
addition, since frothing may occur. Heat the solution to boiling once again with stirring.
Gravity filter the hot solution (Caution! hold the flask with tongs or use a towel) into
another 25 mL Erlenmeyer flask using a short stem funnel or better a stemless one .
Pre-heat the funnel with hot solvent (see Fig. 5.15W).
During the filtration crystals may appear in the funnel due to the cooling or evaporation of the solution. This can often be avoided by pre-heating the funnel or by heating the solution in the receiving flask during the process so that warm vapors envelop the funnel. Once the filtration is complete, add a small amount of hot solvent to the original flask and pass this through the filter.

Concentrate the warm filtrate by heating the flask (add a Si-C stone or stir bar) on a sand bath in the **hood** to the point of where the original volume of solvent used
remains. Allow the flask to cool to room temperature. If crystals do not appear, concentrate the solution further and recool. At this point it may be necessary to add a seed crystal or to scratch the walls of the flask with a glass rod (this is most successful if carried out at the interface of the solution surface with the flask) to induce crystallization. Finally, place the flask and contents in an ice–water bath for 10-15 minutes to complete the crystallization. Recover the crystals by suction filtration using a Hirsch funnel (see Filtration Techniques). Wash the crystals carefully with a small amount of cold 95% ethanol. To do this operation, vent the vacuum pump and add a small amount of ice-cold solvent over the crystals. Drain off the wash by closing the vent and repeat once or twice more, if necessary. Continue to apply reduced pressure to the filter plate to aid in drying the crystals. Determine the melting point and compare it to the literature value. Calculate the percent recovery.

Example [5BW]: Recrystallization of Naphthalene from a Solvent Pair.

Using the equipment and techniques described in the recrystallization of benzoin, dissolve about 200 mg of naphthalene in the minimum amount of warm acetone. Heat the solution to boiling and then slowly add (dropwise) warm water while stirring, until a cloudy solution is obtained. Now add more acetone dropwise until the solution is clear once again. Remove the flask and allow the solution to cool. It may be necessary to scratch the surface of the glass flask with a glass rod or add a seed crystal to initiate crystallization. Further cool the solution in a ice-water bath. Collect the crystals by suction filtration, wash and dry them in the usual manner. Weigh the dried crystals. Calculate the percent recovery. Determine the melting point and compare it to the literature value.