Crystal Growth, Evaluation and Handling

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Whether you are growing your own crystals or giving advice to someone else trying to do so, it is vital to remember that the quality of the crystal from which diffraction data are acquired is generally the main determinant of the final quality of the structure. The effects of a sub-optimal crystal will propagate through data collection, structure solution and refinement to affect the quality of the final structure, in which unsatisfactorily high uncertainties may limit useful comparison and discussion. It may be difficult or impossible to get such a structure published.

Remember: poor crystals → poor data → poor results

Protect your crystals. Before you start trying to grow crystals you need to think about how they will be handled. Rather obviously, they will need to be extracted from the vessel they grew in without suffering any damage. Less obviously, some containers make this easier than others: an oversized 250 ml round-bottomed flask makes the procedure of finding and removing a small crystal unnecessarily difficult. At the other extreme, a container with a small aperture that will not admit a narrow spatula or pipette is also troublesome. You should avoid screw-top or other containers which narrow near the top, as the "shoulders" prevent easy removal of the crystals: a small vial with straight walls works best.

Many crystals lose solvent on removal from the solution in which they have grown (mother liquor). Although the envelope of the crystals may appear intact, even a few percent solvent loss usually renders them useless for structural analysis. This is particularly common for crystals grown from chlorocarbon solvents like dichloromethane and chloroform, but can affect crystals grown from almost any solvent, water included. If a crystal loses solvent and then does not behave well on the diffractometer, there is no way to know whether the original crystal was unsuitable, or whether the poor diffraction was solely due to solvent loss. For this reason you should submit crystals under mother liquor whenever possible. There are other good reasons for doing this - see below.

Crystal Growth. The term recrystallisation has two related meanings but there are crucial differences between these. *In the synthesis and purification of compounds*, the aim is to maximise purity and yield, although these can be mutually exclusive. The material is often precipitated very rapidly (*ca.* 1 second), resulting in microcrystalline or virtually amorphous products that are useless for conventional single crystal work. *For diffraction work* the object is to obtain a small number (one may do) of relatively large (*ca.* 0.1–0.4 mm) single crystals. As long as this is achieved, yield is irrelevant and purity is likely to be enhanced. To this end crystals should be grown *slowly*, taking from minutes to months depending on the system. To understand why this is important, visualise the process of

growth at a crystal surface. The greater the rate at which molecules arrive at the surface, the less time they have to orient themselves in relation to molecules already there: random accretion is more likely, leading to crystals which are twinned or disordered. Suitable growth conditions include the absence of dust and vibration: if these are present they can lead to small or non-singular crystals.

Survey of Methods

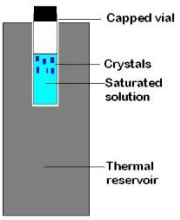
(A) Solution methods

These are by far the most flexible and widely used. They are suitable for use with molecular compounds that are the subject of most crystal structure determinations. The use of solvents means that crystals can grow separately from each other. It is therefore important not to let a solution dry out, as crystals could become encrusted and may not remain single. When choosing solvents remember the general rule that "like dissolves like": look for a solvent that is similar to the compound (in terms of polarity, functional groups, etc) and an anti-solvent that is dissimilar to it in order to reduce its solubility (see below). Information about solvents is available from several sources (e.g. *Handbook of Physics and Chemistry*, chromatographic elution data), and the process of synthesising and purifying a compound will often confer a knowledge of suitable solvents. Mixing solvents allows manipulation of solubility: a mixture of solvent A (in which a compound is too soluble) and anti-solvent B (in which it is not sufficiently soluble) may be more useful than either alone. If crystals grown from one solvent are poor in quality, try different solvents or mixtures of solvents. Solution methods can be extremely flexible: a number of crystallisations, differing in the proportions of solvents A and B used, can be set up to run in parallel. If a particular range of proportions appears to be more successful in producing crystals it can be investigated more closely by decreasing the difference between successive mixtures of A and B.It is important that any vessels used for crystal growth should be free of contaminants. Older containers also tend to have a large number of scratches and other surface defects, providing multiple nucleation points and tending to give large numbers of small crystals. Two factors which favour the formation of twinned crystals are the presence of impurities and uneven thermal gradients. Conversely, if the inner surface of a container is too smooth this may inhibit crystallisation. If this appears to be the case, gently scratching the surface with a metal spatula a few times may be effective. Some of the possible variations are described briefly below, and virtually all methods described can be adapted to accommodate air-sensitivity.

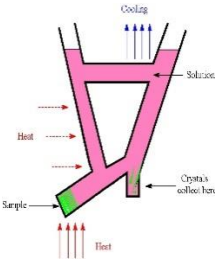
Cooling. *Either* make up a hot, nearly saturated solution and allow it to cool slowly towards room temperature *or* make up such a solution at room temperature and cool it slowly in a fridge or freezer. The cooling rate can be reduced by exploiting the fact that the larger and more massive an object the longer it will take to lose heat. Thus, a hot solution in a large vessel (or in a small vessel within a larger one) will cool relatively slowly. Similarly, a sample tube containing a solution will cool at a slower rate if it is contained in a metal block that was originally at room temperature, or if surrounded by an effective layer of insulation. Cooling methods are based on the generally valid assumption that solubility decreases with temperature. There are rare exceptions to this (*e.g.* Na_2SO_4 in

water) and some solubilities rise so rapidly with temperature that it can be difficult to control crystallisation (*e.g.* of KNO_3 from water). However, it is usually possible to find a combination of solute and solvent where solubility varies slowly and controllably with temperature.

Convection. The aim here is to establish a temperature gradient across the solution, so that material dissolves in the warmer area and deposits in the colder. This gradient can be established by various means, for example (a) allow sunlight to shine on one part of the vessel (b) put one part of the vessel against a cooler surface, such as a window at night (c) construct an apparatus with low-power electrical heating elements in some sections (see



Crystal growth by controlled cooling



An apparatus which exploits convection

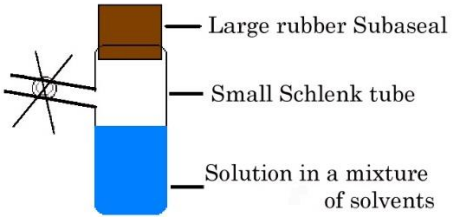
diagram). A smooth concentration gradient will give the best results.

Concentration. If the volume of a solution is reduced, for example by evaporation of a volatile solvent, the concentration of the solute will rise until it begins to crystallise. When using mixed solvents the poorer solvent should be the less volatile so that the solubility of the solute decreases upon evaporation. The rate of evaporation can be controlled in various ways, for example by altering the temperature of the sample or by adjusting the size of the aperture through which the solvent vapour can escape. As solvents are frequently flammable or irritant, it is important to work on the smallest scale possible and ensure than any vapour released from the solution is safely dealt with. Avoid obvious hazards such as those that will arise if large volumes of diethyl ether or other highly volatile solvents are allowed to evaporate in a closed container such as a refrigerator.

As noted above, it is highly undesirable to let a solution evaporate to dryness as this will allow otherwise suitable crystals to become encrusted, grow into an aggregate or be contaminated by impurities. The crystals may be degraded by loss of solvent of crystallisation, especially if chlorocarbon solvents such as dichloromethane have been used. It may prove impossible to identify good crystals even if these are present, and extracting them undamaged from a mass of material may prove difficult or impossible.

Apparently sealed NMR tubes which have been forgotten at the back of a fume cupboard or fridge for weeks or months are a fruitful source of good quality crystals: there is in fact slow evaporation of solvent and crystals are able to grow undisturbed. As long as the NMR

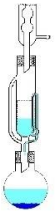
tube is clean and relatively unscratched the smooth inner surface and narrow bore provide an excellent environment for crystal growth.



A method of controlling solubility by selectively removing the less volatile solvent in which the compound is more soluble. This chlorocarbon solvent is absorbed by the rubber Subaseal while the anti-solvent (diethyl ether) is not, leading to a more concentrated solution and eventually to crystallisation.

One method that combines variation of both concentration and temperature and is especially useful for sparingly soluble compounds is Soxhlet extraction. The recycling of the solvent is the key factor here and crystals can even appear in the refluxing solvent. Failing this, they normally appear after slow cooling of the solution. There are several other methods available to control concentration. One of these is based on osmosis, where the solvent passes through a semi-permeable membrane into a concentrated solution of an inert species. The resulting increase in the concentration of the solute may lead to crystal formation.

Solvent diffusion. This method is based on the fact that a compound will dissolve well in certain solvents ("good solvents") but not in others ("poor solvents" or anti-solvents), which must be co-miscible. Dissolve the compound in the "good solvent" and place this solution in a narrow tube. Using a syringe fitted with a fine needle, very slowly inject the neat anti-solvent. If it is lighter than the solution, layer it on top; if it is denser, inject it slowly into the bottom of the tube to form a layer under the solution. Injecting the solvent is better than running it down the side of the tube. If the tube is protected from vibration, these layers will mix slowly and crystals will grow at the interface. If necessary, cooling of the tube can be used both to lower the rate of diffusion and to reduce the solubility.

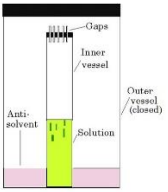


Soxhlet apparatus

Solvent diffusion

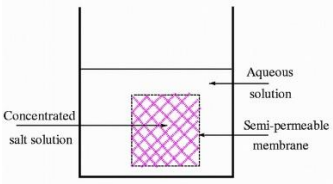
Vapour diffusion. This method is also called isothermal distillation. The anti-solvent diffuses through the vapour phase into a solution of the compound in the "good solvent", thereby reducing the solubility. The advantages of this method include the relatively slow

rate of diffusion, its controllability and its adaptability, for example in combination with Schlenk techniques to grow crystals of air-sensitive samples. It is usually worth trying vapour diffusion as it frequently succeeds where other methods have failed. A variant on this is the hanging drop method, principally used for the growth of crystals of proteins and other macromolecules: the precipitant sits in a well and diffuses slowly into a drop of solution suspended on a glass slide covering the well.

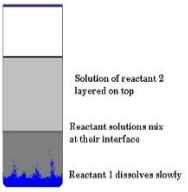


Vapour diffusion

Reactant diffusion. It is sometimes possible to combine synthesis and crystal growth. In favourable cases crystals may simply drop out of the reaction mixture, but the rate of many reactions means that crystals form rapidly and are therefore small and of low quality. If the reaction rate can be controlled by slow addition of one of the reactants this offers one way to overcome the problem. The best control is often achieved by controlling the rate at which reactant solutions mix, by interposing a semi-permeable barrier (*e.g.* membrane, sinter or an inert liquid such as Nujol) or by the use of gel crystallisation (see below). Another variant involves placing a solid reactant at the bottom of a tube, covering it with a solvent in which it is known to dissolve slowly, and carefully adding an upper layer consisting of a solution of a second reactant. The additional time required for the solid to dissolve reduces the rate at which reaction can occur.



Crystal growth by osmosis



Crystal growth by dissolution and mixing

Zeolites and many other materials with network structures cannot be recrystallised and therefore can only be obtained from the reaction mixture. Fine tuning of the reaction conditions and the proportions and concentrations of reactants probably offer the only realistic ways to control crystal size and quality.

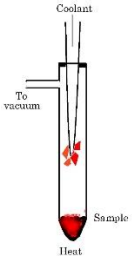
Crystallisation from gels is an under-exploited technique for obtaining single crystals of compounds of low solubility. Because the mixing of the solutions is dominated by diffusion through a viscous medium, undesirable competing processes such as convection and sedimentation are minimised. It is therefore possible to establish laboratory

conditions for crystallisation that closely approximate the microgravity of space. A typical arrangement is a U-tube half-filled with gel, with a solution of one reactant in the top of one arm and a solution of another reactant in the other. As gels are generally colourless it is much easier to detect and isolate crystals of a strongly coloured product. There are various recipes for the preparation of gels: (e.g. http://www.cryst.chem.uu.nl/lutz/growing/gel.html; H. Arend & J.J. Connelly, *J. Cryst. Growth* 1982, **56**, 642) and it is possible to treat gels with organic solvents to produce versions suitable for use with hydrophobic or moisture-sensitive compounds.

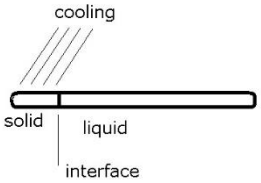
Seed Crystals. Sometimes crystallisation of a compound gives crystals which, although otherwise of good quality, are clearly too small for structure analysis. A small number of these can be used as seeds by placing them into a warm saturated solution of the compound and allowing the solution to cool slowly. The hope here is that crystal growth will occur preferentially at the seed to give a suitably large single crystal. A container free of contaminants and scratches is strongly recommended here.

(B) Sublimation

Sublimation is the direct conversion of a solid material to its gaseous state. It has been harnessed to produce solvent-free crystals of electronic materials but it is applicable to any solid with a significant vapour pressure at a temperature below its decomposition or melting point. The basic experimental arrangement is simple: a closed, usually evacuated vessel in which the solid is heated (if necessary) and a cold surface on which crystals grow. If possible avoid heating the solid, as lower sublimation temperatures often lead to better crystals. If the solid sublimes too readily the vessel can be cooled. If a compound has a low vapour pressure, sublimation can be enhanced by evacuating the vessel or by using a cold finger containing acetone/dry ice (-78°C) rather than cold water (5–10°C).



Sublimation



Basic method for *in situ* crystal growth

(C) Fluid phase growth

It is possible to grow crystals directly from liquids or gases, often by employing *in situ* techniques. Fluid phase methods encompass both high temperature growth from melts and low temperature growth from compounds that melt below ambient temperature. High temperature methods (Bridgman, Czochralski, zone refining, etc) are used widely in the purification and growth of crystals of semiconductors and other electronic materials but are limited to compounds that melt without decomposition, thereby excluding many molecular compounds. Moreover, it is much more difficult to prevent unwanted

phenomena such as twinning than with solution methods, and often impossible to separate overlapping or adjacent crystals. Liquids or gases must be contained, for example in a capillary tube. One consequence of this is that crystallisation conditions must be controlled to give only one crystal in that part of the tube that will be within the *X*-ray beam. Once crystals have grown it is usually impossible to separate them physically. Unlike crystal growth from solution there is essentially only one variable, namely the temperature of the sample. However, there are several ways to do this and the method can be chosen to give coarse or fine control. A typical strategy for crystal growth involves the establishment and manipulation of a stable interface between liquid and solid phases. With air-stable compounds that crystallise in a fridge or freezer it is only necessary to keep them cold until they are transferred into the cold stream of the diffractometer's low temperature device.

(D) Solid-state synthesis

In favourable circumstances it may be possible to produce adequate single crystals, but microcrystalline samples are far more typical. For example, most high T_c superconductors do not give single crystals and their structures have been determined using powder diffraction methods. As with the synthesis of zeolites from solution, variation of synthetic conditions is likely to be the only route to better single crystals.

(E) General comments.

The details of crystal growth are often poorly understood, especially for new compounds, and it is important not to be discouraged if initial attempts fail. For example, microcrystalline material is not immediately useful but it does indicate that the compound is crystalline and that modification of the crystallisation technique could result in larger crystals. It is always a good idea to try a range of techniques, keeping a detailed record of the exact conditions used and the results obtained. This not only allows identification of the most promising methods and conditions for the current sample but also means that in future there will be database of procedures and their outcomes to consult. Crystal quality improves with experience, and early attempts often produce poor quality crystals. It is important to continue until it is clear that no further improvement is likely.

In some cases, regardless of the method employed, crystals either do not form or are unsuitable. At this stage, the best way to proceed may be to modify the compound. With ionic compounds it may be practical to change the counterion (e.g, BF_4^- for PF_6^-, or *vice-versa*). With neutral compounds it may be a simple matter to change some chemically unimportant peripheral group. In one case altering a piperidine substituent to morpholine, which merely involves changing one remote CH_2 group for an oxygen atom, led to a spectacular improvement in crystal quality.

Evaluation

Once crystals have appeared it is necessary to ascertain whether they are suitable for data collection. Some of the methods used are extremely rapid and can save large amounts of diffractometer time. During these procedures take care to prevent damage to the crystals, for example by loss of solvent after removal from the mother liquor. If spare crystals are available, leave one or two exposed on a microscope slide and check them regularly for signs of deterioration, using microscopy as described below. It is vital to apply the tests

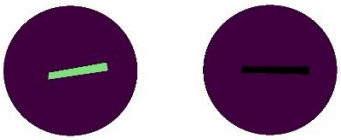
outlined below *optimistically* so that only crystals that are incontrovertibly unsuitable are rejected. Any that give uncertain indications of their quality should be given the benefit of the doubt.

1. Microscopy. Visual examination under a microscope takes only a few seconds or minutes, yet can identify unsuitable crystals that might otherwise occupy hours on a camera or diffractometer. A microscope with a polarising attachment, up to x40 magnification, a good depth of field and a strong light source is required. Crystal examination consists of three steps.

STEP ONE: With the analyser component of the polarising attachment out (*i.e.* not in use) look at the crystals in normal light to determine if they are well-shaped. Reject crystals that are curved or otherwise deformed, have significant passengers which cannot be removed, or that show re-entrant angles. Be wary of rejecting crystals simply on the grounds that they are small, unless similarly sized crystals of the same type of compound have not previously been successful. For organic compounds containing no element heavier than oxygen, crystals smaller than 0.1 x 0.1 x 0.1 mm^3 seldom give good data with conventional laboratory instruments, although this size may be ideal for crystals of an osmium cluster compound.

STEP TWO: With the analyser in, most crystals in a typical sample will transmit polarised light. The exceptions are tetragonal and hexagonal crystals viewed along their unique *c* axis, and cubic crystals viewed in any orientation. Tetragonal or hexagonal crystals transmit polarised light when viewed along other directions but cubic crystals cannot be distinguished from amorphous materials such as glass by this method. Fortunately, these three crystal systems together account for less than 5% of molecular crystals.

STEP THREE: If a crystal transmits polarised light, turn the microscope stage until the crystal turns dark (extinguishes), then light again, a phenomenon that will occur every 90°. This extinction is the best optical indication of crystal quality, and it should be complete throughout the crystal and be relatively sharp (*ca.* 1°). Any crystal that does not extinguish completely is not single and can be rejected immediately. Lack of sharpness may indicate a large mosaic spread within the crystal. A crystal that never extinguishes is almost certainly an aggregate of smaller crystals. When examining a batch of crystals, establish both the general quality of the sample and whether there are individual crystals suitable for further study.



Optical extinction observed between crossed polars

2. X-ray photography. Photography began to decline in popularity as data collection using four-circle instruments advanced, in part because it is often quicker to record a full dataset is than to obtain a complete set of photographs. Photography retained

the advantage that it gave a better view of the reciprocal lattice than can be obtained from the list of reflections output by a four-circle diffractometer, and can record any diffraction occurring at other than the expected positions. Other than for specialist applications, the spread of area detector instruments finally consigned X-ray photography to history. Area detector images give much the same view of the reciprocal lattice as film, but do so much more quickly, flexibly and precisely without the need to process film.

3. Diffractometry. The ultimate test of a crystal is how it behaves on the diffractometer. Reflections must possess sufficient intensity, be well-shaped (not split or excessively broadened) and index to give a sensible unit cell. Area detector instruments combine some of the best features of photographs and electronic counters and some can establish the quality of a crystal in seconds. It is worth bearing in mind that area detectors can often tolerate crystals of apparently appalling quality.

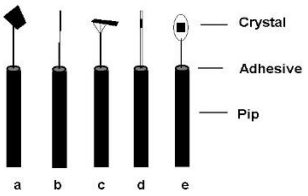
Crystal Mounting

Standard procedures

For crystals that are stable to ambient conditions of air, moisture and light the requirements of mounting are simple. The crystal is fixed securely with a reliable adhesive (*e.g.* epoxy resin) onto a glass or quartz fibre that is in turn glued into a "pip" which fits into the well at the top of the goniometer head. The aim is to ensure that the crystal does not move with respect to this head. This means rejecting adhesives that do not set firmly (*e.g.*, vaseline or Evo-Stik) or mounting media that are not rigid (*e.g.*, plasticine, Blu-tack or picene wax). On some diffractometers crystals are spun at up to 4000°/minute, and an insecure mounting will lead to serious problems of crystal movement. A suitable fibre (*e.g.*, of Pyrex glass) is just thick enough to support the crystal at a distance of about 5 mm above the pip. Fibres that are too thick add unnecessarily to errors *via* absorption and background effects, while those that are too thin can allow the crystal to vibrate, especially if it is being cooled in a stream of cold gas. For normal-sized crystals, the fibre should be thinner than the crystal. For small or thin crystals use a "two-stage" fibre, which consists of a glass fibre onto which is glued approximately 1 mm of glass wool to which the crystal is attached. The fibre confers stability while the short length of glass wool reduces the amount of glass in the X-ray beam.

This paragraph outlines the basic procedure for mounting a crystal. First mix the epoxy resin which will typically become tacky within five minutes and thereafter remain useable for a further five. Place the tip of the fibre into the resin and use the microscope to check that it has actually become coated. Ideally, the aim is to attach the tip of the fibre to the side of the crystal, thereby minimising the amount of glass in the X-ray beam. Establish the size of the crystals, cutting them to size with a scalpel or razor blade if necessary. When picking up a crystal there is a danger of gluing it onto the slide, but this can be easily avoided. Move the adhesive tipped fibre forward until it makes contact with the side of the crystal, then continue moving the fibre forward and upwards to lift the crystal clear of the slide. [With thin plates this procedure may not be possible. If there is no alternative to mounting a crystal with a fibre along an edge or across a face of the crystal the fibre must be as thin as possible: a "two-stage" fibre may be appropriate.] Also make sure that the

crystal height can be adjusted to bring it into the X-ray beam: it is frustrating to find later that this cannot be done due to a fibre that is too long or too short – on many instruments the X-ray beam passes 68 mm above the upper surface of the φ circle.
Instead of a simple fibre, some crystallographers prefer to mount the crystal on the end of a capillary tube (less glass in the beam for the same diameter); on a number of short lengths of glass wool attached to a thicker fibre (ditto); or on quartz fibres (more rigid for a given diameter).



Some methods for mounting crystals: a) on a glass fibre; b) on a "two-stage" fibre; c) on a fibre topped with several short lengths of glass wool; d) within a capillary tube; e) in a solvent loop.

Air-sensitive crystals

The traditional way to protect sensitive crystals is to seal them (using a flame or epoxy resin) into a capillary tube, usually made from Lindemann glass which is composed of low molecular weight elements. Even so, this puts a large volume of glass in the X-ray beam, so the tube and wall diameters should be as thin as practicable. The most sensitive crystals can be handled and encapsulated within a dry box. When planning a low temperature data collection, ensure that the top end of the tube is well rounded and that there are only a few millimetres of glass above the crystal position, otherwise severe icing will result (alternatively, see the second paragraph following). Crystals that desolvate may need either solvent vapour or mother liquor sealed into the tube with them. Unless crystals are mechanically robust, care must be taken when loading them into capillary tubes. With crystals that are both fragile and susceptible to solvent loss, a variant of a technique used by protein crystallographers may be helpful. Break the sealed end off a capillary tube and coat the first few millimetres of its inner surface with freshly-mixed epoxy resin; place some crystals with their mother liquor in a well and isolate a good crystal; bring the open end of the tube through the surface of the solution; it may take some practice, but capillary action should draw the crystal along with some mother liquor into the tube; the crystal will stick to one side of the tube, which can then be sealed at both ends.
Many crystals can be protected by coating them with materials such as nail varnish, superglue or epoxy resin. As long as the coating confers sufficient protection and does not react with the crystal, this can be a simple and effective solution to air-sensitivity that is applicable when cooling of the crystal is impossible. This situation can arise because a phase change is known or suspected to occur below ambient temperature, or because cooling causes an unacceptable degree of mechanical strain within the crystal.

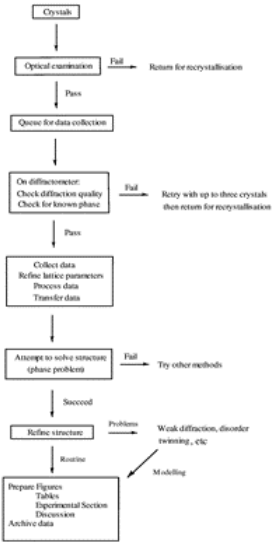
A low temperature device permits the use of an extremely flexible method for handling air-sensitive crystals. This involves transferring, examining and mounting the crystal under a suitably viscous oil. Upon cooling, the oil forms an impenetrable film around the crystal and also acts as an adhesive to attach the crystal firmly to the fibre. For crystals that do not survive room temperature, the technique can be combined with low-temperature handling, which normally involves passing a stream of cold nitrogen gas across the microscope stage. Various oils have been used but perfluoropolyethers have the advantages of inertness and immiscibility with solvents. The excellent Riedel de Haen RS3000 is no longer produced, but one alternative is PFO-XR75, available from Lancaster Synthesis, although it is not quite so inert and has a lower viscosity. For many crystals silicone grease will be an adequate substitute.

An alternative method, popular with protein crystallographers and suitable for very thin crystals that are too fragile to be picked up on a fibre, is the solvent loop. A small loop of a fibre such as mohair or a single strand from dental floss is used to lift the crystal in a film of solvent or oil that is then flash cooled on the diffractometer to immobilise the crystal (for more details see E.F. Garman & T.R. Schneider, *Journal of Applied Crystallography* 1997, **30**, 211--219). MiTeGen MicroMounts™ and MicroLoops™ (see http://www.mitegen.com) provide more robust, reusable alternatives.

The final step is to attach the goniometer head to the φ circle of the diffractometer and optically adjust the crystal so that its centre does not move when it is rotated. Do not assume that the microscope cross-hairs represent the true centre, although if the instrument is reasonably well set up this should be a useful starting point. Centring is an iterative procedure, and the following outline should be generally applicable to many instruments:

- Check that the crystal is *approximately* central in *X* and *Y* by checking at φ = 0, 90, 180 and 270° then set the height *Z* approximately.
- View the crystal at φ 0 and 180°, then at 90 and 270°. At each position any lateral offset must be the same as that 180° away.
- Optionally, on an instrument with a fixed χ circle the height *Z* can be checked by rotating ω through 180°; with a motorised χ circle the height is checked at χ = -90 and +90°.
- Repeat the two previous steps until convergence is achieved.

Procedure for crystal evaluation



Some References on Crystal Growth and Handling

Peter G. Jones, "Crystal Growing", *Chemistry in Britain* 1981, 222–225.
[This article also covers aspects of crystal evaluation and is highly recommended.]
H.E. Buckley, "Crystal Growth", Wiley (London), 1951.
[Very detailed, good for background and a source of alternative ideas for growing crystals but strangel there is almost no mention of sublimation.]
T. Köttke and D. Stalke, *Journal of Applied Crystallography* 1993, **26**, 615–619.
[**The** paper on the use of oil films for handling sensitive crystals. Excellent on practical aspects].
P.M. Dryburgh, B. Cockayne and K.G. Barraclough (eds.), "Advanced Crystal Growth", Prentice Hall International (UK) Ltd, 1987. (ISBN: 0-13-011249-6).
Look at the literature on related compounds: at the very least, authors should have identified the solvent they used and the temperature at which crystals were grown.
Some crystal growing hints and tips on the Web
http://xray.chem.uwo.ca/crystal_growing/GrowXtal.html
http://www.oci.uzh.ch/group.pages/linden/sample_prep.html
http://www.cryst.chem.uu.nl/lutz/growing/growing.html
http://www.cryst.chem.uu.nl/lutz/growing/gel.html
http://www.southampton.ac.uk/xray/links/crystalgrowth/grow1.htm
http://www.nottingham.ac.uk/~pczajb2/growcrys.htm