Synthesis and Solid State Pharmaceutical Centre (SSPC)

National Crystal Growing Competition

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SYNTHESIS AND SOLID STATE PHARMACEUTICAL CENTRE

Innovation Through Collaboration

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Competition Overview

The aim of the competition is for an individual student to grow a single crystal using either Salt (Sodium Chloride), Alum, Sugar, or Copper Sulphate (to be used only with instructions from your teacher in school), which will be judged by SSPC experts on crystallisation and crystallography.

Who can participate?

The competition is open to students of primary and post-primary schools in Ireland. There are two categories, one for primary and one for post-primary. There will be one overall winner from each category. Teacher supervision is required for crystallisation of compounds other than salt or sugar. Please download the Material Safety Data Sheets for Health and Safety instructions and indications for materials from the SSPC website www.sspc.ie/crystal_growing.

Prize

- Primary Category: iPad Mini
- Post Primary Category: iPad Mini

How to register:

- Download the instructions and work with your teacher in your school and e-mail (sspccrystals@gmail.com) or tweet (#sspc_crystals) if you have any questions, and start growing your crystal!

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- Once you have grown your crystal and are ready to submit to the competition, tweet us with a picture of your crystal using the hashtag #sspc_crystals. Then email (sspccrystals@gmail.com) with a high resolution image of your crystal, along with the following details:
    - The county you live in
    - The name of your school
    - Your Class/Year in school
    - Your age
    - Your name
    - Weight of Crystal in grams/milligrams (as accurate as possible)
    - Any further remarks on growing the crystal, challenges, highlights etc

Materials to crystallize, you can choose from any of the following:

- Sodium Chloride (Salt): NaCl, Solubility: 35.9 g/100 mL (20°C, water).
    - NaCl tends to form smaller crystals, or less well formed crystals because the solubility barely changes at all as a function of temperature; at 20°C, one can dissolve 35.9g of NaCl in 100g of water, and at 100°C, just 39.2g per 100g of water. The most appropriate method of growing sodium chloride crystals is therefore by evaporation of a saturated solution. Small (sub-millimetre) clear cubes with smooth faces will grow on the bottom of your glass dish or jar, or on any thread suspended in the jar. Larger crystals tend to develop hopper faces, or even more erratic growth habits. One interesting experiment to try is to see how the growth morphology changes if you add

small quantities of other substances - a smidge of copper sulfate perhaps, K-alum, or sodium nitrate - to your saturated salt solution.

- Potassium Aluminium Sulphate (Alum), $KAl(SO_4)_2.12H_2O$, gives transparent octahedral crystals. Solubility: 11.8g/100 mL (20°C, water). Teacher supervision required, see MSDS.
- Copper (II) Sulphate Pentahydrate: $CuSO_4.5H_2O$, gives blue crystals. Solubility: 32 g/100mL (anhydrous, 20°C, water). Teacher supervision required, see MSDS.
- Sucrose (table sugar or known as saccharose), $C_{12}H_{22}O_{11}$: Solubility: 211.5 g/100 mL (20°C, water).
  - Cane sugar produces great crystals without too much trouble, provided you can be patient. Dissolve ~500 grams of sugar per 100 mL of hot water, and leave to cool. The pale silvery-yellow solution is very viscous when supersaturated, and can take from a week to over a month to start producing crystals, depending on how big a jar you're using. Crystals shoot from smaller volumes of liquid quite quickly and can grow to a length of a few millimetres. Use these as seeds to grow much larger crystals. You can grow very pretty single crystals over a period of just a few weeks. Sucrose is slightly deliquescent; in other words, the crystals 'sweat' a bit. You'll find the crystals become slightly moist and sticky, even when you've dried them, particularly in a warm room.
- Ammonium Magnesium Sulfate Hexahydrate, $(NH_4)2Mg(SO_4)_2.6H_2O$, gives transparent long crystals. Teacher supervision required, see MSDS.

    - The crystallization is started from ammonium sulfate and magnesium sulfate. Dissolve at room temperature equivalent amounts of both salts in water (e.g. 0.4 mol of both compounds in 45-48 mL water). Stir until everything is dissolved. Now make the solution supersaturated by adding small amounts (2 to 5 gram) of both salts under gentle heating (max. 30-40 °C). Cover the beaker and allow to cool at room temperature. Now proceed with the crystal growth in the usual way.

- Magnesium Sulphate (known as Epsom salts), $MgSO_4$/ $MgSO_4.H_2O$, gives clear needle like crystals. Teacher supervision required, see MSDS.

- Copper Acetate Monohydrate $Cu(CH_3COO)_2.H_2O$. The recipe below gives blue-green monoclinic crystals. Solubility: 7.2 g/100mL (20°C, water). Teacher supervision required, see MSDS.

    - Dissolve 20 grams of copper acetate monohydrate in 200 mL of hot water. If a scum of undissolved material persists, add a few drops of acetic acid and stir well. Cover this solution, and allow it to cool and stand for a few days; usually it will deposit crystals spontaneously.

- Potassium Sodium Tartrate (Rochelle Salt) of $KNaC_4H_4O_6.4H_2O$, gives transparent long crystals. Solubility: 63 g/100mL (anhydrous, 20°C, water). Teacher supervision required, see MSDS.

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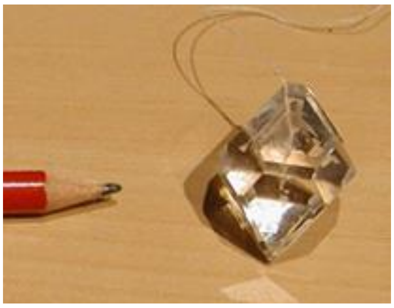
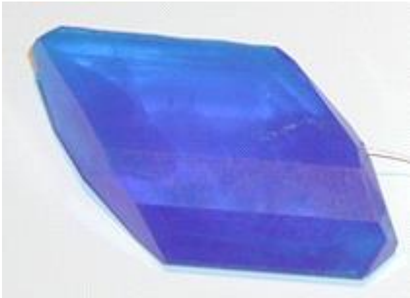
Salt crystal, credit: picture by Luc Van Meervelt

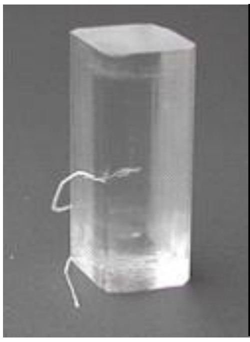


Alum crystal, credit: picture by Luc Van Meervelt



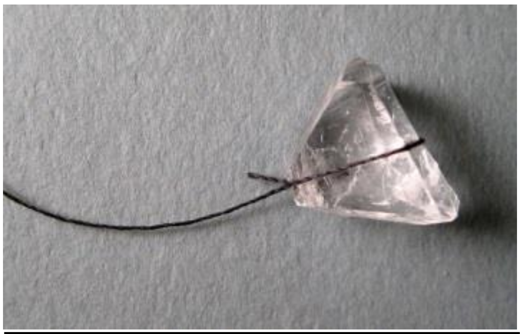
Copper Sulphate crystal, credit: picture by Luc Van Meervelt

Sugar crystal, credit: picture: http://www.solarnavigator.net/solar_cola/sugar.htm



Potassium Sodium Tartrate, ‘Rochelle Salt’ crystal, Credit: picture by Luc Van Meervelt

Ammonium Magnesium Sulfate Hexahydrate Crystal, Credit: picture by Luc Van Meervelt



Magnesium sulphate ‘epsom salt’ crystal, Credit: http://skywalker.cochise.edu/wellerr/crystalgrow/how-form.htm

Copper Acetate Monohydrate crystal, Credit: picture by Coba Poncho

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Closing date and finalist event

- Closing date for submissions is 30th January 2015.
- The judges will pick a number of finalists to visit the Synthesis and Solid State Pharmaceutical Centre for Engineers Week, 8th -14th February 2015.
- The finalists will be invited to bring their crystal to be displayed at the Synthesis and Solid State Pharmaceutical Centre, hosted at the University of Limerick. The winner will be announced publicly at this event and the prize will be awarded.

Judging Criteria

The judging will be on single crystal quality and e-mail submission. Judging criteria for crystal:

- well-defined, flat, smooth crystal faces (out of 2)
- clarity (out of 2)
- Size – the crystal should be visible to the naked eye (out of 2)
- Total Observed Quality Q = x.xx (out of 6)

The Total Score is then determined as follows:

- Total Score = [log (M+1)] x Q

- The logarithm of the mass is chosen so that large poor quality crystals don't swamp out smaller good quality crystals.
- The value 1 is added to the mass so that crystals weighing less than 1 g get a positive score.

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How to grow your crystal

Growing a beautiful crystal takes time and an almost daily follow-up. The idea is to grow a single crystal, not a bunch of crystals. You will first need to grow a small perfect crystal, your seed crystal, around which you will later grow a large crystal. It is therefore essential to avoid excessive rapid growth, which encourages the formation of multiple crystals instead of a single crystal.

What you need:

- Substance to be crystallized
- Distilled or demineralized water
- A small wood rod, popsicle or sate stick
- A shallow dish (*e.g.* Petri dish)
- Thermometer
- Balance
- Plastic or glass container
- Heating plate
- Beaker of 2 to 4 litres volume
- Fishing line (1 to 2 kg strength)/ fine strong thread/fine strong string
- Superglue
- Styrofoam box or picnic cooler
- A magnifying glass

Stage 1: Grow a seed crystal

- Warm about 50 mL of water in a glass container.
- Dissolve a quantity of the substance to produce a saturated solution at the elevated temperature.

- Pour the warm solution into a shallow dish.
- Allow the solution to cool to room temperature.
- After a day or so, small crystals should begin to form as in Figure 1.
- Remove some of the crystals.
- With a magnifying glass select a beautiful and transparent small crystal. This will be your seed crystal. Weigh the crystal.

Figure 1. Seed crystals of alum. (Credit: picture by Luc Van Meervelt)

Stage 2: Grow a large Single crystal

- Glue the seed crystal at the end of a piece of fishing line/thread by using superglue (be careful not to glue your fingers together!).
- Check with the magnifier that the seed crystal is well-fixed to the line.

To grow your large, single crystal, you will need a supersaturated solution.

> *We all know that sugar dissolves in water. At 40° C 250g of sugar will dissolve in 100mL of water. This value is called the SATURATION Solubility of sugar in water at*

40 ˚C. If you add more sugar at this temperature is will not dissolve, but remain in suspension, even with vigorous stirring.

BUT, how do you get sugar to crystallise or recrystallize? The trick is to quickly cool the saturated solution. Suppose we cool it quickly to 15˚ C. At this temperature the water is only able to dissolve 200g of sugar in 100mL of water. However, the extra dissolved sugar, in this case 50g per 100mL, remains dissolved for a short time, and during this time we have a supersaturated solution.

The "extra" sugar (50g per 100mL) crystallises out of solution and the sugar-water mixture returns to its saturated state. This technique produces a large number of small crystals.

A saturated solution is one in which no more solute can be dissolved in the solvent. For example if you add sugar to water until no more will dissolve you then have a saturated solution

So then a super saturated solution is one where there are more particles or solutes than solvent in the solution. So how can we make one of these? If we add sugar to water until no more can dissolve we will have a saturated solution, to make this solution supersaturated we can heat the solution to a certain temperature and then continue to add sugar. This is because as we increase the temperature in this case it will allow more sugar to dissolve, thus making our solution supersaturated.

The amounts of substance and water to be used will depend upon the solubility at room and elevated temperatures. You may have to determine the proper proportions by trial and error (just like the first scientists did!).

- Place about double the amount of substance that would normally dissolve in a certain volume of water at room temperature into that volume of water. (e.g. If 30 g of X dissolves in 100 mL of water at room temperature, place 60 g of X in 100 mL of water.) Adjust the proportions depending upon how much material you have. Use clean glassware.

- Stir the mixture until it appears that no more will go into solution.
- Continue stirring the mixture while gently warming the solution.
- Once all of the substance has gone into solution, remove the container from the heat.
- Allow the solution to cool to room temperature.
- You now have a supersaturated solution. Allow to cool to room temperature.

An alternative method to create a supersaturated solution is:

- to start with a saturated solution and let the solvent evaporate. This will be a slower process. A third method is given below:
- Select an appropriate volume of water.
- Warm this water to about 15–20° C above room temperature.
- Add some of your substance to the warm water and stir the mixture to dissolve completely.
- Continue adding substance and stirring until there is a little material that won't dissolve.
- Warm the mixture a bit more until the remaining material goes into solution.
- Once all of the substance has gone into solution, remove the container from the heat.
- Allow the solution to cool to room temperature.
- You now have a supersaturated solution.

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Now you are ready to grow a large single crystal starting from your seed crystal.

- Carefully suspend your seed crystal from the stick into the cold supersaturated solution in the middle of the container with supersaturated solution (Figure 2).
- Cover the container in which the crystal is growing with plastic wrap, aluminium foil or a piece of cardboard in order to keep out dust, and reduce temperature fluctuations.

Figure 2. Seed crystal of alum suspended in saturated solution. (Credit: picture by Luc Van Meervelt)

The solubility of some salts is quite sensitive to temperature, so the temperature of recrystallization should be controlled as best you can. It is possible that you have a nice big crystal growing in a beaker on a Friday, the room temperature raising in a school over the weekend, and by Monday morning the crystal had totally gone back into solution. So it is a very good idea to place your growing crystal inside a Styrofoam box (Figure 3) or picnic cooler!

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Figure 3. Styrofoam or isomo box.

- Observe the crystal growth. Depending upon the substance, the degree of supersaturation and the temperature, this may take several days before the growth slows down and stops.
- Resupersaturate the solution. This may need to be done on a daily basis, especially when the crystal gets larger. But first, remove the crystal.

Determine the weight of the crystal and compare it to the previous weight. Make your solution again supersaturated by adding the amount the crystal grew. Warm and stir the solution until everything is gone into solution. Cool the solution to room temperature!

- Each time the solution is saturated, it is a good idea to ‘clean’ the monocrystal surface, by
    - making sure the crystal is dry;
    - not touching the crystal with your fingers (hold only by the suspending line if possible);
    - removing any ‘bumps’ on the surface due to extra growth;
    - Removing any small crystals from the line.

It is a good habit to clean your hands after each manipulation.

- Re-suspend the crystal back into the newly supersaturated solution.
- Repeat the previous steps as needed.

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Frequently asked questions

Why does the crystal stop growing?

A crystal will only grow when the surrounding solution is supersaturated with solute. When the solution is completely saturated, no more material will be deposited on the crystal. (This may not be entirely true. Some may be deposited; however an equal amount will leave the crystal surface to go back into solution. We call this an equilibrium condition.)

Why did my crystal shrink/disappear?

If your crystal shrank or disappeared, it was because the surrounding solution became under saturated and the crystal material went back into solution. Under saturation may occur when the temperature of a saturated solution increases, even by only a few degrees, depending upon the solute. (This is why temperature control is so important.)

How do I get crystal growth restarted?

Make the solution supersaturated again!

Help, my crystal has lost its transparency!

When removing the crystal from the solution, clean it very quickly in water to rinse the thin layer of solution on the crystal surface away. Otherwise this thin layer would leave an amorphous (non-crystalline) precipitate on the surface after evaporation. This will decrease the transparency of the crystal, and you will not be able to harvest a perfect transparent crystal as in Figure 4.

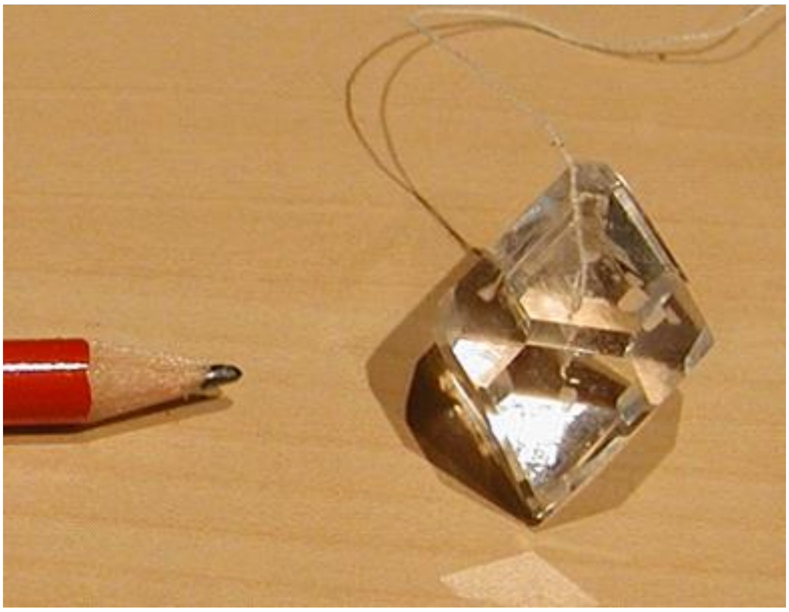

Figure 4. Transparent alum crystal. (Credit: picture by Luc Van Meervelt)

What is the difference between an under saturated, saturated and supersaturated solution?

In recrystallization, one tries to prepare a solution that is supersaturated with respect to the solute (the material you want to crystallize). There are several ways to do this.

One is to heat the solvent, dissolve as much solute as you can (said to be a "saturated" solution at that temperature), and then let it cool. At this point, all the solute remains in solution, which now contains more solute at that temperature than it normally would (and is said to be "supersaturated").

This situation is somewhat unstable. If you now suspend a solid material in the solution, the "extra" solute will tend to come out of solution and grow around the solid. Particles of dust can cause this to occur. However this growth will be uncontrolled and should be avoided (thus the recrystallization beaker should be covered). To get controlled growth, a "seed crystal", prepared from the solute should be suspended into the solution (Figure 5).

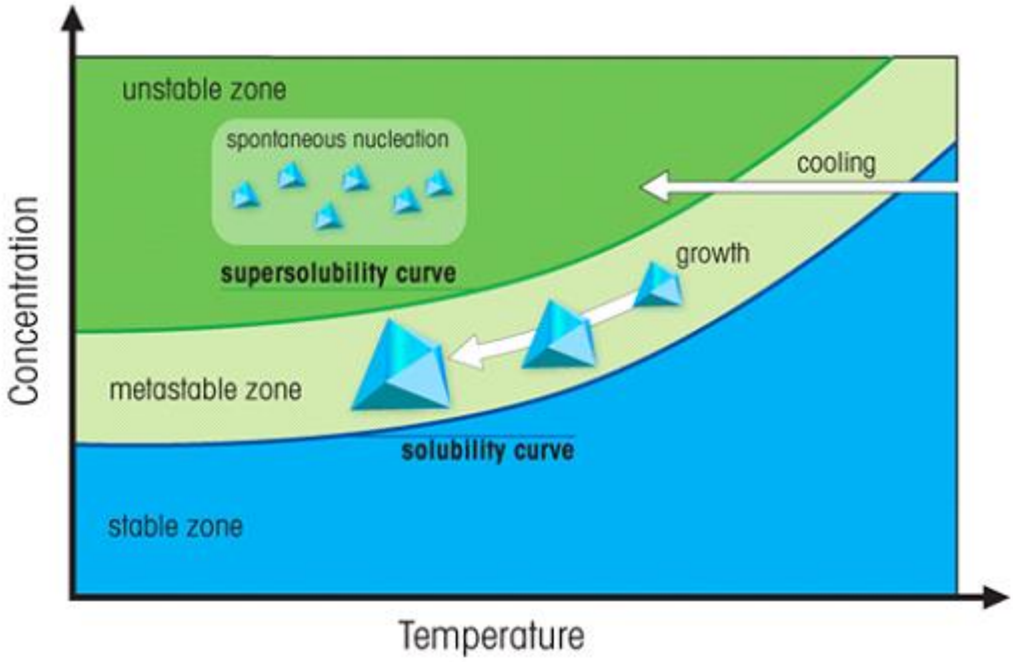

Figure 5. The region above the solubility curve is the called "supersaturated". In the unstable zone (green) spontaneous nucleation occurs. A crystal suspended in the metastable zone will grow further.

The supersaturation method works when the solute is more soluble in hot solvent than cold. This is usually the case, but there are exceptions. For example, the solubility of table salt (sodium chloride) is about the same whether the water is hot or cold.

Can I prepare a supersaturated solution in a different way?

A second way to get supersaturation is to start with a saturated solution and let the solvent evaporate. This will be a slower process. A third method is given below:

- Select an appropriate volume of water.
- Warm this water to about 15–20 deg above room temperature.
- Add some of your substance to the warm water and stir the mixture to dissolve completely.
- Continue adding substance and stirring until there is a little material that won't dissolve.
- Warm the mixture a bit more until the remaining material goes into solution.
- Once all of the substance has gone into solution, remove the container from the heat.
- Allow the solution to cool to room temperature.
- You now have a supersaturated solution.

I am a perfectionist, can I do anything else?

To get improved symmetry and size, slowly rotate the growing monocrystal (1 to 4 rotations per day). An electric motor with 1 to 4 daily rotations might be difficult to find (consider one from an old humidity drum-register or other apparatus). This option becomes useful only when a monocrystal gets rather big. You can also place the beaker into a thermostated bath set to a few degrees above room temperature.

Slow or fast growing, what is the best?

The rate at which crystallization occurs will affect crystal quality. The more supersaturated a solution is, the faster growth may be. Usually, the best crystals are the ones that grow slowly.

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What is the effect of impurities?

Once you have mastered the crystal growth, you may be interested in trying to grow single crystals in the presence of introduced ‘impurities". These impurities may give different crystal colours or shapes.

Does this method also work for proteins?

No, it is not possible to make a supersaturated protein solution by dissolving protein into a hot solvent. The protein will denature and loose its regular folded structure. A special set-up is needed here. In the hanging drop method (Figure 6) for example, a droplet containing protein, buffer and precipitant is hanging above a larger reservoir containing buffer and precipitant in a higher concentration. As water evaporates from the droplet it will transfer to the reservoir where it is bound to the precipitant. During this process the protein is concentrated. Once supersaturation is reached, nucleation and crystal growth is starting.

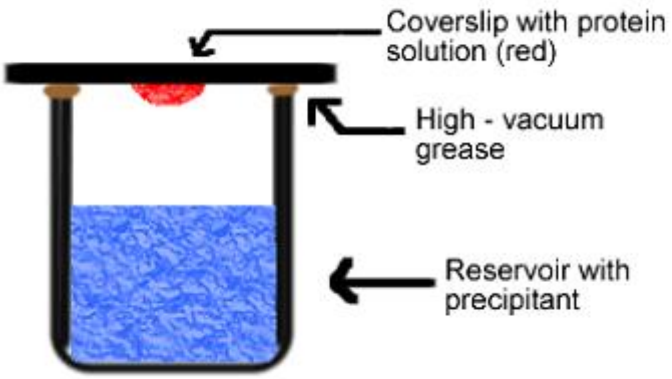

Figure 6. Hanging drop vapour diffusion method for protein crystallization. (Rhodes, Gale. Crystallography Made Crystal

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Contact SSPC

To find out more information contact the SSPC Education and Outreach Officer Dr Sarah Hayes: sarah.hayes@ul.ie

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