






Crystal-growing competition



for UNESCO Associated Schools



2014

United Nations
Educational, Scientific and
Cultural Organization

International
Union of
Crystallography

international year of
crystallography

Partners for the International Year of Crystallography 2014

A major objective of the International Year of Crystallography is the establishment of a vibrant worldwide network of schools participating in crystal-growing experiments and taking part in national and regional competitions, to introduce students to the exciting, challenging and sometimes frustrating world of growing crystals. More information about the International Year of Crystallography is available at www.iycr2014.org.

To celebrate this initiative, the International Union of Crystallography (IUCr) organizes a worldwide competition in 2014, open to all schoolchildren (whether involved in a national competition or not). The winners, will be those who most successfully convey their experiences to the panel of judges through videos or essays. More information about this competition is available at www.iycr2014.org/participate/crystal-growing-competition.

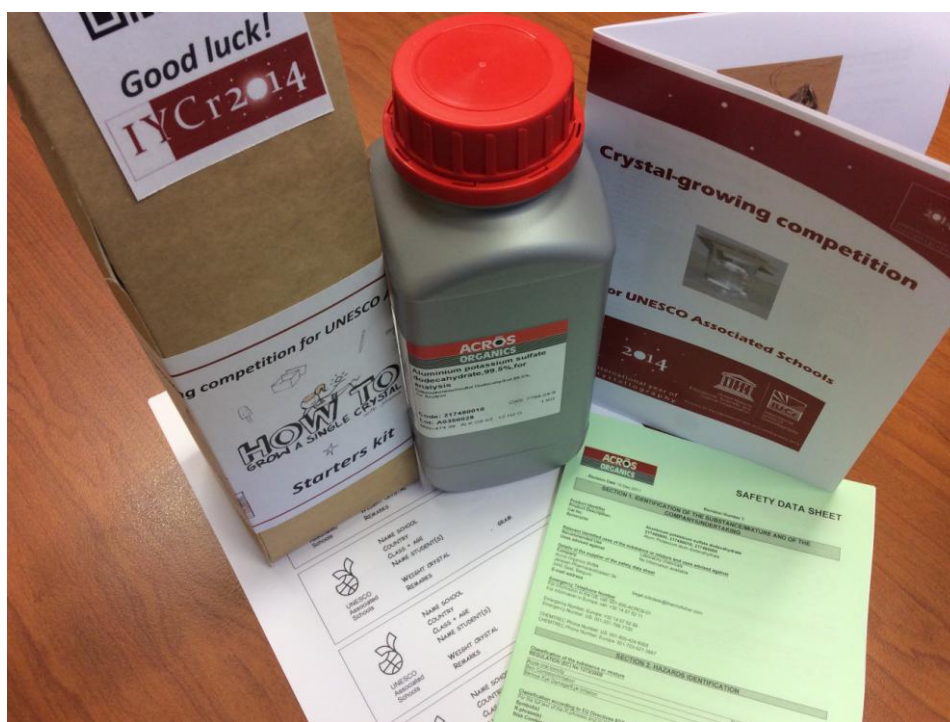
At the same time the International Union of Crystallography organizes together with UNESCO a special crystal growing competition for selected schools belonging to the UNESCO Associated Schools network. Selected schools receive a starters kit containing some documentation and 1 kg alum, the material to crystallize during this competition. In this brochure we provide information to teachers and schools who participate in this exciting venture.

Good luck with the crystallization experiments!

Jean-Paul Ngome Abiaga, Luc Van Meervelt, Michele Zema

1. Welcome to the IUCr-UNESCO crystal-growing competition!

For many years crystal growing competitions have been run successfully in a number of countries. The International Year of Crystallography in 2014 provides perfect timing to start new competitions worldwide. For a number of selected UNESCO Associated Schools the International Union of Crystallography and UNESCO have developed a starters kit containing a brochure, labels, a materials data safety sheet (MSDS) and one kilogram alum or potassium aluminum sulfate, the compound to crystallize during this competition. We encourage you to film the crystallization experiments. These videos can not only participate to the worldwide crystal-growing competition, but can also be used in other schools in your country which at the moment do not have the possibility to get familiar with crystallization experiments.



Credit: picture by Luc Van Meervelt

Important dates

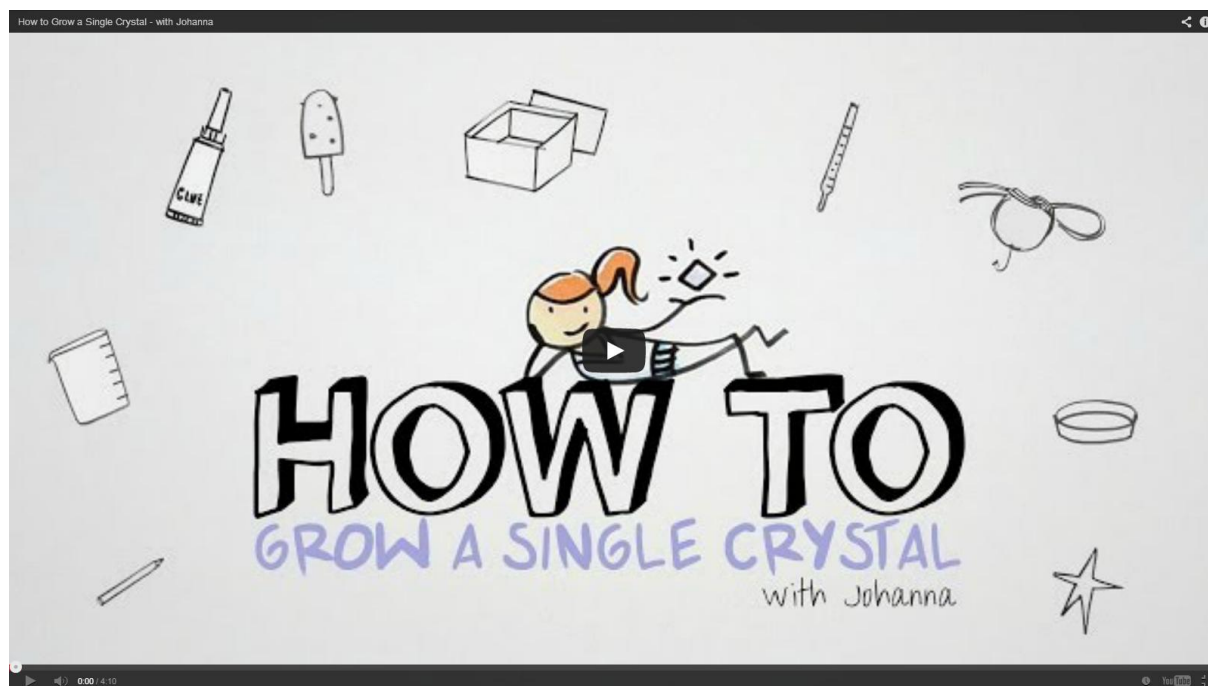
You have received this kit beginning September 2014 and are expected to prepare your students for the competition during the remaining weeks of September. The official start of the competition is **Monday 6 October 2014**. During a period of four weeks your students should grow a single crystal of alum. We recommend to work in groups of 4-6 students which makes the daily follow-up of the crystallization process easier. The competition ends on **Friday 31 October 2014**. Crystals should reach the UNESCO headquarters before **15 November 2014**. The laureates of this competition will be announced during the first half of December 2014.

2. How to Grow Crystals

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 (alum)
- 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)
- Superglue
- Styrofoam box or picnic cooler
- A magnifying glass



Watch our video '*How to grow a single crystal*' on
<http://www.iycr2014.org/participate/crystal-growing-competition>

Important things to know in advance!

- How much alum you have to work with, which you can determine by weighing it on a balance.
- The solubility of the substance in water at room temperature, which you can obtain from a chemistry reference book.
- It would also be useful to know the solubility of the substance at elevated temperatures, which is information that may also be available in a reference book such as *Handbook of Chemistry and Physics*. Figure 1 shows the solubility of alum as function of the temperature.

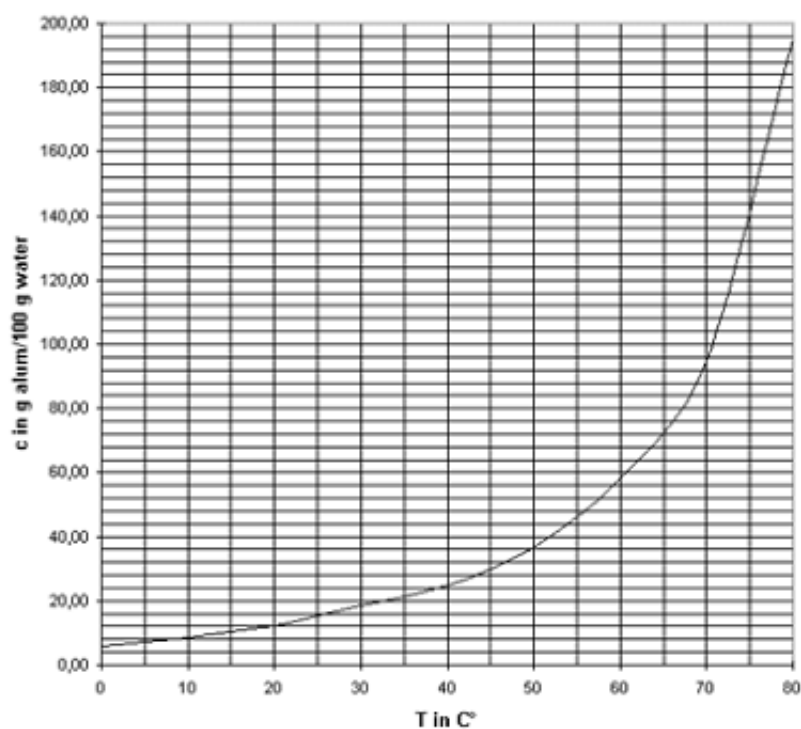


Figure 1. Solubility of alum in water as function of temperature. (Credit: http://www.crystalgrowing.com/alte-version/recipes/solution_calculator/solution_calculator.htm)

Of course, you need to make a careful assessment of any risk or safety precautions associated with the material you plan to use. For example,

- check the safety data sheet supplied with any chemicals;
- ensure that children are aware of the dangers of hot plates, or of mounting materials such as superglue;
- use safety glassware and other appropriate laboratory equipment;
- provide lab coats, gloves and safety goggles as appropriate.

The protocol!

First Stage: 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 2.
- 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 2. Seed crystals of alum. (Credit: picture by Luc Van Meervelt)

Second Stage: Grow a Large, Single Crystal

- Glue the seed crystal at the end of a piece of fishing line 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.

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.

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 3).
- Cover the container in which the crystal is growing with plastic wrap, aluminum foil or a piece of cardboard in order to keep out dust, and reduce temperature fluctuations.



*Figure 3. 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 rising 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 4) or picnic cooler!



Figure 4. 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.

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

Some FAQ's

Why does the crystal stop growing?

A crystal will only grow when the surrounding solution is supersaturated with solute. When the solution is exactly 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 undersaturated and the crystal material went back into solution. Undersaturation 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 again supersaturated!

Help, my crystal loses 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 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 5.

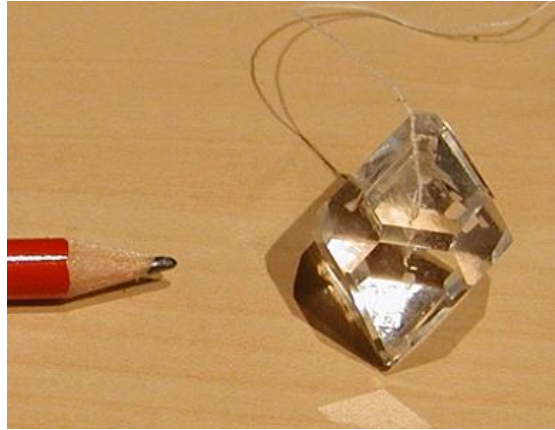


Figure 5. Transparent alum crystal. (Credit: picture by Luc Van Meervelt)

What is the difference between an undersaturated, 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 6).

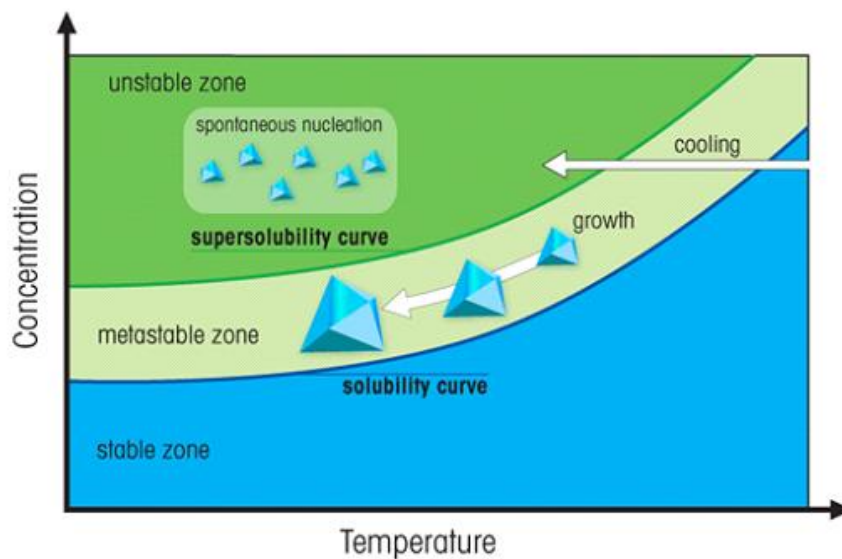


Figure 6. The region above the solubility curve is the called "supersaturated". In the unstable zone (green) spontaneous nucleation occurs. A crystal suspended in the metastable zone will grow further.

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, what can I do additionally?

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.

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 lose its regular folded structure. A special set-up is needed here. In the hanging drop method (Figure 7) 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.

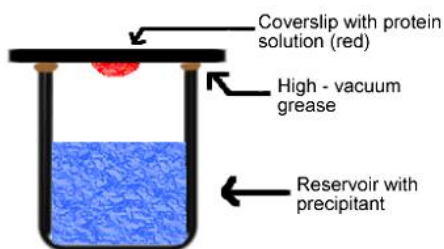



Figure 7. Hanging drop vapour diffusion method for protein crystallization. (Rhodes, Gale. *Crystallography Made Crystal Clear*. San Diego: Academic Press, 1993)

3. How to submit your crystals?

Each single crystal should be packed individually in a **plastic bag**. Attach a label (included in starters kit) to the remaining piece of fishing line. The **label** should contain the name of the school, names of the participants and weight of the crystal (should be more than 0.5 g to be eligible for judging, will be checked!).

| | | |
|--|--|--------|
|  UNESCO Associated Schools | NAME SCHOOL COUNTRY CLASS + AGE NAME STUDENT(S) | |
| | WEIGHT CRYSTAL REMARKS | . GRAM |

Put all your single crystals in a solid cardboard box and send it via UNESCO channels back to the headquarters in Paris:



Jean-Paul NGOME ABIAGA, Ph.D
 UNESCO
 Natural Sciences Sector (Phone Ext: 83891)
 SC/PCB/IBSP
 7 Place de Fontenoy, 75007 Paris
 France

The crystals should arrive in Paris before **15 November 2014!**

4. How are the single crystals judged?

Single crystals will be judged on the basis of combining mass and quality factors as outlined below.

The quality is judged by experts who will rank the crystals on a scale of 0 to 10. A score of 10 will be given to a perfect gem-quality crystal that fits the ideal crystal structure known for the chemical.



Credit: picture by Dirk Poelman

1. The crystal is weighed, and the mass M recorded. The crystal must be a minimum of 0.5 g to be eligible for judging.
2. The quality of the crystal is judged on a scale of 1 to 10, with 10 representing a perfect crystal. The following factors will be considered in judging quality:
 - match/mismatch with crystal type (out of 2)
 - presence/absence of occlusions (out of 2)
 - intact/broken edges (out of 2)
 - well formed/misformed faces (out of 2)
 - clarity/muddiness (out of 2)Total Observed Quality $Q = x.xx$ (out of 10)
3. The Total Score is then determined as follows:
Total Score = $[\log (M+1)] \times Q$
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.

5. More about crystals and alum

For more information on crystals and crystallography, please consult the following links...

Crystallography matters! (20-page booklet describing the role of crystallography in the modern world and the significance of the International Year of Crystallography)

http://www.iycr2014.org/__data/assets/pdf_file/0010/78544/220914E.pdf

Timelines of Crystallography (interactive timelines for Nobel Prizes, Man's fascination with crystals, structure determination, and diverse fields of crystallography)

<http://www.iycr2014.org/timeline>

Learn about crystallography through watching (video clips, webcasts, television programmes and films that explain crystallography)

<http://www.iycr2014.org/learn/watch>

The fascinating world of crystallography! (video prepared for IYCr2014)

<http://www.youtube.com/watch?v=AIBPajICFIU>

Crystallography (educational website about crystals, diffraction and crystal structure determination)

<http://www.xtal.iqfr.csic.es/Cristalografia/index-en.html>

More about alum

Alum is in fact a class of double sulfate salts with chemical formula $AM(SO_4)_2 \cdot 12H_2O$, where A is a monovalent cation and M a trivalent metal ion. The most common representative is aluminum potassium sulfate dodecahydrate, also known as "Alum", "Potassium Alum" or "Potash alum" and has the chemical formula of $KAl(SO_4)_2 \cdot 12H_2O$. This compound will be used during this crystal-growing competition. In nature it is known as the mineral kalinite. Alums can be prepared by dissolving equal amounts of the two salts potassium sulfate and aluminum sulfate in water and to crystallize from this solution. This gives typical transparent octahedral crystals. Solubility: 118 g/L (20°C, water), melting point: 92-93 °C, boiling point: 200 °C.

Safety information is available from the Materials Safety Data Sheet (MSDS) for alum present in your starters kit.

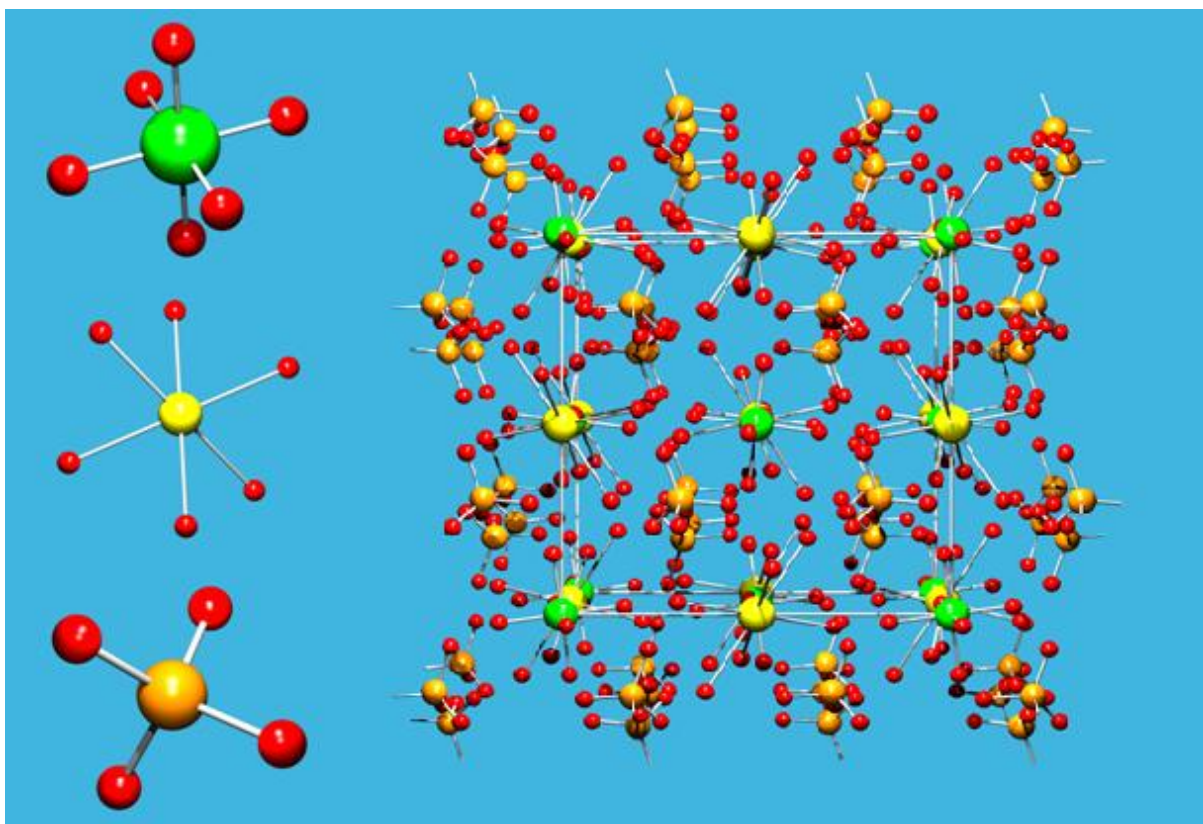


Credit: Wikipedia

Alum is used as blood coagulant (shaving alum) and due to its antiperspirant and antibacterial properties also in underarm deodorants. In the kitchen it is a popular ingredient for pickling and in baking powders. Alum is used in the tanning of animal hides and to fix pigments on a surface such as paper. During the treatment of wastewater, alum is added as chemical flocculant allowing small charged particles to stick together after which they can be filtered from the liquid.

Potassium alum crystallizes in the cubic crystal system with the unit cell parameter a equal to 12.158 Å (1 Å or 1 Ångström is 10^{-10} meter or 0.000000001 meter). The aluminum atoms are situated at the vertices and in the middle of the faces of this cube. Each aluminum atom is coordinated by six water molecules. This coordination is called octahedral as the six oxygen atoms of the water molecules form an octahedron with aluminum at its center. The oxygen-aluminum distances are 1.98 Å.

The potassium atoms are situated at the center and in the middle of the edges of the cube. Each potassium atom is also coordinated octahedrally by six water molecules, but with a longer oxygen-potassium distance of 2.94 Å. The ionic radius of potassium (1.33 Å) is much larger than that of aluminum (0.50 Å). As the radius of lithium (0.60 Å) is too small to realize this packing, lithium alum is not existing. Between both types of octahedrons which occur alternately in the stacking, there are the sulfate groups.



Building blocks and unit cell of aluminum potassium sulfate dodecahydrate $KAl(SO_4)_2 \cdot 12H_2O$ (Al green, red, S orange, K yellow, unit cell and bonds in gray, hydrogen atoms not shown, credit: picture by Luc Van Meervelt)

6. Participate also to the IYCr crystal-growing competition for schoolchildren!

The aim of the competition is to grow your own crystals and to convey your experience through a video or essay. The following guidelines are applicable:

- for a video contribution: maximal duration of three minutes, format mpeg, avi or mov
- for an essay contribution: maximal length five pages, PDF format obligatory

Each contribution should clearly show or mention the experimental work carried out by the participants during growing their single crystals (compounds and methods used are free of choice). Furthermore the contribution should reflect in a creative way on the experimental work and theoretical background and/or applications.

Rules

- Closing date for submissions is **15 November 2014**.
- The competition is open to students of primary or secondary schools; the maximum age is 18.
- Language: mother language of participant or English.
- A maximum of one entry may be submitted by any individual or team (essay or video).
- Contributions must respect the category guidelines (see above) and must be submitted in digital form only by using the Web form located at the address below.
- The judging panel will be nominated by the International Union of Crystallography. The decisions of the judging panel are final.

Submit your entry direct from the Web by following [this link](http://www.iycr2014.org/participate/crystal-growing-competition/submit-entry):

<http://www.iycr2014.org/participate/crystal-growing-competition/submit-entry>

Prizes

The winning contributions in each category will receive 'Young crystal growers' certificates and exciting prizes to stimulate further interest in science.

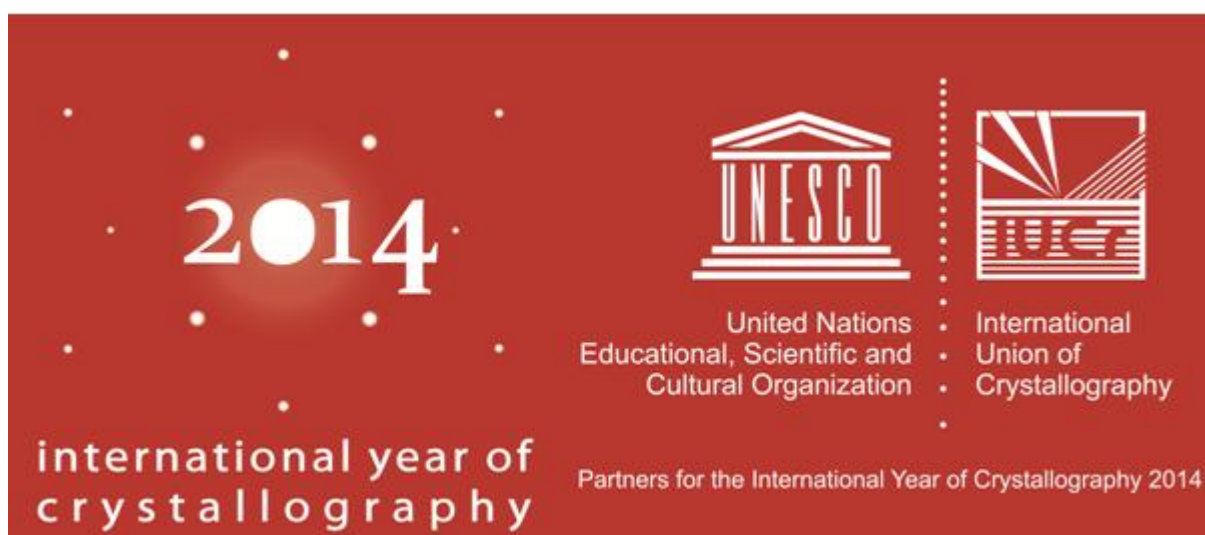
Criteria for evaluation

A panel of judges will evaluate the entries in two different categories. The following criteria will be used: creativity, aesthetic value, description of working plan and experimental work, clarity of explanations and scientific background.

Do you need more support?

The organizers of the current regional and national crystal growing competitions are available for further support. Please contact Luc Van Meervelt (Luc.VanMeervelt@chem.kuleuven.be), Jean-Paul Ngome Abiaga (jj.ngome-abiaga@unesco.org or Michele Zema (mz@iucr.org) for more details.

We are grateful for most of the information in this brochure to the organizers of the Canadian, Belgian, Singapore, Spanish and Australian Crystal Growing Competitions.



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