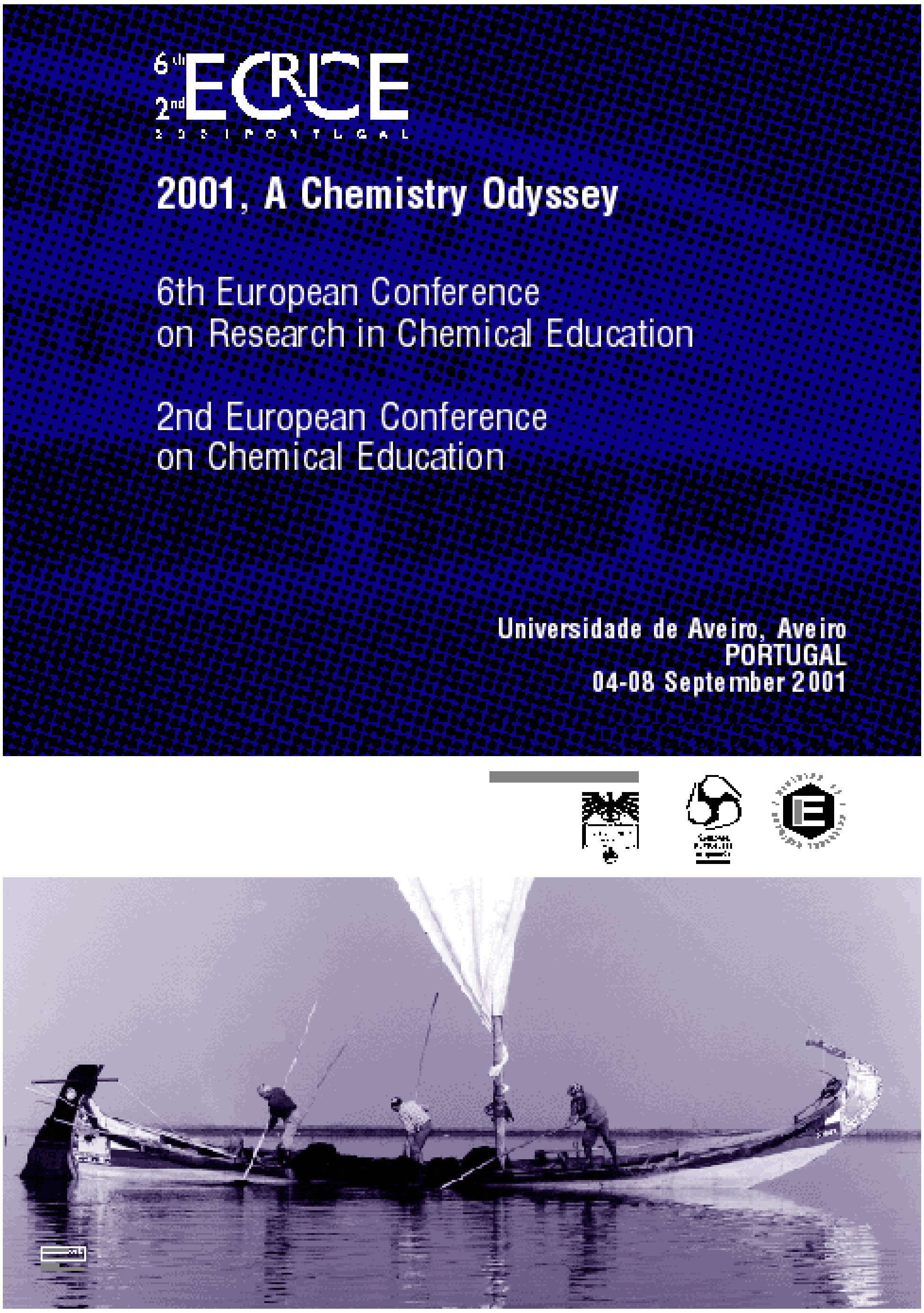

Clementina Teixeira, **Vânia André, Ana S.D. Ferreira, Elsa do Lago, M. Fernanda N. N. Carvalho, "On the Rocks...Occlusion of Dyes in Transparent Inorganic Crystals", poster 10, Proceedings of the 6th European Conference on Research in Chemical Education, 2nd European Conference on Chemical Education, A. F. Cachapuz ed., Universidade de Aveiro, 4-8 September 2001 (Copyright ©ECRICE, 2001).**

ABSTRACT

"On the Rocks...Occlusion of Dyes in Transparent Inorganic Crystals"

Clementina Teixeira, Vânia André, Ana S.D. Ferreira, Elsa do Lago, M. Fernanda N. N. Carvalho

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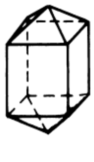
Rough surfaces such as those on rocks, minerals and shells are known to induce crystal growth at lower concentrations and supersaturation degrees, compared to techniques using a seed of the compound immersed in an homogeneous solution. This method based on heterogeneous nucleation also enables the production of more "perfect" single crystals, of higher dimensions and diversity of habits, depending on the reactions or interactions established between the substrate and the solute solution. Since 1994, a wide number of substances were investigated by our group using the so called "On The Rocks" method, and among the most curious examples are ADP and KDP, ammonium (or potassium) dihydrogen phosphates. The pure compounds and habit modifiers were extensively studied by conventional seed growth techniques in isothermal conditions during the seventies, as these are important substances used as transducers for electronics and components for non linear optical devices. Our research on these compounds has mainly the goal to exploit the beauty of the crystals for teaching purposes, their prompt response to selected habit modifiers and capability to be colored by ordinary food colorants and other dyes. Actually, together with potassium alum, which shows identical versatility, ADP is the component sold in kits for crystal growing for children above eight years old. The diversity of colors and shapes of the crystals is very attractive and the preparations are safer than those using inorganic metallic pigments to produce colored specimens imitating minerals and gems.

For the pure ADP the results obtained for rocks and shells used as habit modifiers are in agreement with published data. To our knowledge, no data on food dyes for ADP has ever been published. Some of the dyes can also act as habit modifiers. Data on the compounds, dyes and crystal morphology is presented in this work, including safety rules.



The "perfect" habit, tetragonal prism tapered by a pyramid (below) is obtained using calcium carbonate rocks and shells (oyster, murex, marble) as substrates. Concentrations should always be

lower than 45g/100 ml water for ADP (nucleation starts to increase rapidly). The best range is 37-40 g /100ml. In the absence of a seed crystal or rock fragment crystals are generally tabular. Rates of growth are always higher for ADP compared to KDP. Crystal growth is **much enhanced by granite** (prismatic crystals and tapered prisms) and **by volcanic rocks** (only thin needles, whiskers, are obtained). Only ADP is successfully colored by food dyes.

List of food dyes (1g of commercial dye powder dissolved in 100 ml of warm water).

Ponceau 4R (carminic acid) (red) **Carmoisine** (red-brownish)**Amaranthe** (red)

Indigo carmin (blue-violet) **Tartrazine** (yellow) **Sunset Yellow FCF** (orange)

Green S (light blue, decomposition golden brown product) **Brilliant Blue FCF** (intense blue)

Green crystals are obtained by mixture of colorants (**tartrazine + Brilliant Blue FCF**)

Literature

Teixeira, C. (2000) Os Cristais no Ensino e Divulgação da Química, *Colóquio Ciências*, Fundação Calouste Gulbenkian, 25, 20-36. References cited therein.

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Key words: crystal growth on rocks, synthetic "minerals", heterogeneous nucleation, giant crystals, ammonium dihydrogen phosphate

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This work was published in 2001, in a CDROM of the Proceedings of a Conference in Aveiro, Portugal. It is a review concerning crystal growth on rough surfaces, the method "On the

Rocks" published for the first time in 1994. It comprehends the growth of crystals of ammonium di-hydrogen phosphate (ADP) and potassium di-hydrogen phosphate (KDP), coloured by several food dyes.

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Full Text

"On The Rocks...Occlusion of Dyes in Transparent Inorganic Crystals"

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Figure1- Cluster of acicular transparent crystals (needles C) of ammonium dihydrogen phosphate (ADP) on granite, containing inclusions of iron.

Introduction

The method **"On the Rocks"** for crystal growth has been investigated by us since 1994 [1]. It is partially described in this paper and some references are given [2-4]. A large amount of inorganic (or organic) compounds are enabled to crystallize from supersaturated aqueous solutions on rocks, minerals and other rough surfaces (shells, metal wires, etc., Box 1), simulating in a very simple way some of the processes involved in the genesis of minerals in Nature. The beauty of the single large crystals produced by this method strongly motivates the students to go further in their studies on crystal growth and many other related subjects.

Main details of the method of crystal growth "On the Rocks"

There are four major variables to consider in this method, as illustrated in Box 1:

1-The best substances for "easy" crystal growth: those that afford giant single crystals or clusters by very simple techniques within short to medium periods of time (from several hours up to a couple of weeks).

2-The materials with rough surfaces used as hosts for stimulating crystal growth (Boxes 1, 2):

a) They provide a large quantity of particles in suspension to induce nucleation (heterogeneous nucleation).

b) They offer a rough surface with lots of small ledges, pits, holes, steps and kinks to protect the nuclei being formed from small microscopic aggregates (illustrated in the drawing at right).

c) Attractive forces may be established between the substrate and the solute, enhancing the crystal growth rate. It was proved that lower supersaturation degrees (GS) [2-4] are required in this case, compared to the growth from a seed (the thread method or equivalent) [2,3].

3- The reactions or interactions between the two groups of substances. Particularly interesting are habit modifications discussed in this work for **ADP** (Figs.1, 2) and **potassium dihydrogen phosphate (KDP)** [4].

4- The best techniques for crystal growth. Within this report, just supersaturation processes in aqueous solution will be addressed: slow cooling (for substances with solubility increasing with the temperature) and controlled evaporation (see the solubility data for ADP and KDP in Appendix).

Box 1- Major components for the "On the Rocks" Method

SUBSTANCES

Elements: S_8 (molecular crystals), Cu, Ag, Pb, Sn (metallic crystals)

Compounds: Inorganic ionic salts, other inorganic and organic compounds, complexes, etc.

⇑

REACTIONS or OTHER INTERACTIONS (Such as habit modifications)

⇓

HOST MATERIALS always with rough surfaces

Metal wires, pipe cleaners, tissues, wood, branches of trees, ceramic objects, glass

ROCKS and MINERALS **SHELLS**

CRYSTALLIZATION TECHNIQUES, mainly in solution: cooling of saturated and insaturated solutions, with supersaturation and precipitation of solute/ evaporation of the solvent.

Solvents - **Water,** alcohol, acetone, others

The general method to prepare any "On the Rocks" specimen or "synthetic mineral" is the following:

a) Heat (60-70°C) and stir a concentrated solution of the substance under study (water-soluble compounds, with solubility increasing with the temperature, Fig. 3). The concentration should be optimized in advance for each solute: it depends on the mean room temperature of the laboratory during the growth and also on the host chosen.

b) Introduce the rock fragment or shell carefully into the beaker (immerse completely in the solution).

c) Cover the beaker with plastic film to reduce evaporation. Leave it to cool undisturbed as slowly as possible (inside a warm water bath, to produce thermal inertia). Choose a place where room temperature is nearly constant.

d) After 1-2 days, make some holes in the film or remove it completely to allow evaporation of the solvent.

e) Wait for a few days. Use a pencil lamp to check the size of the crystals without disturbing them.

f) Remove the rock or shell with the crystals when they are big enough.

g) Recover the solution, by filtration, for other preparations or dry it for later use.

h) Wash the crystals gently with iced water. In some cases additional washing with ethanol, improves the drying step. Try first with one crystal, in order to verify that is a convenient washing solvent.

i) Dry the crystals in cold air and protect them with a layer of nail polish.

j) Keep them inside a transparent plastic or glass box sealed with silicone wax. Protect from light, dust, heat and humidity. Do not forget to label the box.

A technical sheet (Table 1) should be filled during the laboratory work. This form can be simplified for primary school students. Plot the solubility of the compound as a function of temperature. Represent the initial and final concentrations of the preparation (Fig. 3). Make some comments on the results obtained for the composition of the solution after crystal growth. The crystals look like minerals and gems. Verify the analogies, and indicate how to distinguish them from the real ones.

For safety reasons do not use metallic containers for the preparations, as they might not be inert and react with the solutions. Glass is ideal for this type of work. The hosts (Box 2) should be cleaned previously, using methods according to their composition [2-4]. Big rocks should be broken with a hammer (use a piece of cloth for cover). ***Don't forget the safety rules given in the final remarks of this text.***

Reprinted from ref.4: TEIXEIRA, C. (2000) Os Cristais no Ensino e Divulgação da Química. Colóquio Ciências, 25, 20-36.

Figure 2-Left: the perfect form of pure ADP single crystals - tetragonal prism + pyramid (A). Center: squeme of the evolution for the perfect habit A, to tapered prism + pyramid B and finally, needles or whiskers C Right: acicular crystals C of ADP grown on volcanic rocks. The samples shown in both photographs are transparent.

Table 1 - Data collection during the experiment

Start Date:	End Date:
Mass of beaker (empty)/g	Total mass (beaker, solution, host and crystals)
Mass of solute No1/g-	Mass of water lost by evaporation
Mass of solute No2/g-	Mass of crystals grown out of the host rock/g
	Mass of crystals on host rock/g
Mass of host rock or shell/g	Total mass of crystals/g
	Final concentration of solution
Classification of rock or shell	Period of crystal growth
Volume of water /ml	Was there any reaction or interaction with the host ? Why?
Volume of solution/ml	Dimensions of crystals, maximum / minimum
Total mass/g (beaker + solution + host)	Crystal system/Habit
Temperature for dissolution/ ° C)	Final solution temperature/° C(interruption of growth)
Room temperature / ° C	Room temperature /° C
pH	Ph

Box 2-Hosts for heterogeneous nucleation, "On the Rocks" method *(Best samples in bold).*

Host Rocks with rough surfaces

Magmatic or igneous rocks

Intrusive	**Extrusive**
granite, feldspathic and quartz rocks or quartz (silica-rich rocks, acid rocks)	*basalt, pumice*, **pyroclastic rocks, effusive rocks, volcanic tuffs**

Sedimentary rocks

sandstone, arenites, conglomerates, limestone

Metamorphic rocks

quartzite (formed from arenites) gneiss and marble (calcite)

Artificial Hosts (Rocks or other)

concrete, cement, ceramics, gypsum, bricks, **rough glass**

Other Hosts

Wood: cones, branches; tissues: wool, flannel, tow; **metals: wires, grid, pipe cleaners**

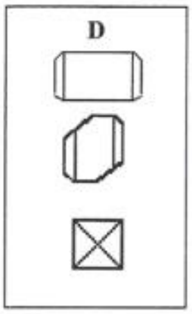
Shells with rough surfaces

Murex, oyster shells, rough shells in general, corals, sea-urchins, sea-horses

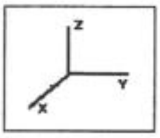
ADP and KDP, a very interesting application "On the rocks"

In General Chemistry text books crystallization and crystal growth techniques are often neglected, although we live in a world surrounded by crystals. The few exceptions mention crystal growth of hydrated copper sulfate and potassium alum, prepared from a seed by the thread method, by cooling/evaporation of saturated solutions. Recently, our work was for the first time cited in the literature by Kotz et al [5]. We ignore that other groups, beyond our followers, are applying it as a teaching method.

An extensive search [1-3] gave information on many other substances suitable for crystal growth by this technique of heterogeneous nucleation. ADP and the isostructural KDP salt (Figs.1, 2) are excellent for demonstrating this method. Moreover, they are related to modern technology, as components for optoelectronics (piezoelectricity, transducers, devices based on non-linear optics, etc.) and they provide excellent examples for teachers that wish to illustrate the relevance of laboratory work on crystal growth, in what concerns modern industrial applications. In addition, some of these technologies are based on physical properties that can be evaluated in crystals grown by students, e.g. piezoelectricity (Rochelle's salt $KNaC_4H_4O_6.4H_2O$, ADP, KDP) and duplication of frequency by laser irradiation in non-linear optics (ADP, KDP, urea). The industrial production of both the bulk chemicals ADP and KDP has also presented some problems that fostered the research on crystal growth of these compounds. Mullin and co-workers reported in the seventies [4, 6] that crystals of these two substances are prone to undergo several habit modifications (forms A, B and C, Fig.2; tabular prismatic forms, drawing D). The crystal habit is strongly dependent of the crystallization conditions, *i.e.* the presence of habit modifiers (including H_3O^+), the degree of supersaturation of the solution (GS), rate and method of crystal growth (cooling or evaporation), etc.. The experimental conditions should therefore be strictly controlled during the growth to optimize the morphology, according to the application of the crystals.



Large, perfect and transparent single crystals of type A (Fig.2) are important in certain domains of physics and optoelectronics. They are formed by fast growth in the X, Y directions, that can be achieved in two ways:



a) Using high GS, though kept below the onset of the nucleation, avoiding the formation of small crystals in large number. b) Buffering the pH of the solutions slightly above 4.2, by addition of NH_3 or $(NH_4)_2HPO_4$. The pH effect can be explained by a complex mechanism of H_3O^+ ions adsorption on selected faces, decreasing their growth. On the other hand, the crystals transparency is affected by impurities trapped from the solvent, which might occur as inclusions (entrapment of impurity or solvent into the structure of the crystal) or occlusions (surface fluid becomes trapped between agglutinated crystals). Both phenomena can occur simultaneously and are increasing with the rate of crystal growth. Therefore, optimization of GS is necessary in order to get both the habit A and the required transparency. Veils are also defects frequently observed in this form (Fig.2), caused by variable growth rates. In spite of these difficulties, the world's largest fast-growth crystal ever produced by man is a KDP specimen of type A, weighing 701 pounds [7]!

Tapered prism + pyramid B crystals are favored by faster growth in the Z direction. This form is obtained from low GS, with enhanced transparency, or by addition of traces of metal ions with different angles of tapering θ, M^{III} (M = Cr, Fe, Al, etc., θ_{max}= 18 °, M= Cr). In this case the hydrated complexes $[M(H_2O)_6]^{3+}$are the active habit modifiers. In the limit, needles or whiskers C are formed, when the concentration of these species reaches a critical value. Form C should be avoided in the fabric of microcrystalline bulk chemicals ADP and KDP (Table 2), as they have the tendency for caking and have poor flow properties, handling and packing. The iron (III) ions generated during the flow of the ADP and KDP acidic saturated solutions (Table 2), through the steel tubing of industrial plants, were the first habit modifiers studied. This event fostered the research on crystal growth for these two compounds. Finally, different prismatic tabular habits can be obtained (drawing D) by evaporation of unseeded solutions.

The wide variety of possible applications for ADP and KDP promoted the study of these compounds, and their characteristics are well known (Tables 2, Fig.3, Appendix), as well as the methods for growing their crystals. Both compounds are cheap and non-toxic substances, easy to handle even by students at primary schools (above eight years old). Several applications related to these compounds are described below.

The pure compounds ADP and KDP "on the rocks"

Crystals of ADP or KDP (Panreac) were grown from aqueous solutions (concentrations ranging from 37g up to 55g per 100 ml distilled water) according to the method described above. The pH (~4) of the solutions was checked, in order to verify which of the phosphates (mono- or dihydrogen) were used, since the diammonium and dipotassium salts form basic solutions, pH~8. The different trade names of these solutes (Table 2) frequently cause some misunderstanding. The initial composition for some of the preparations with KDP were plotted in Figure 3, together with the solubility data from the Appendix. The initial points (40g of salt/100ml water, corresponding to 28.6% mass) are scattered indicating different heating periods. The scattering of the final points, around the equilibrium line for saturated solutions, is a common trend for very soluble compounds used in this method, as discussed elsewhere [2-4]. The best results were obtained removing completely the plastic film from the beaker (step d), allowing for slow evaporation after the cooling period, until we got a convenient size for the crystals being grown. However, the evaporation of water should be controlled to prevent creeping of the solution (uncontrolled evaporation till dryness produces dendrites, "chemical trees", when hosts like volcanic rocks are used). The concentrations corresponding to the final points were corrected for the mass of evaporated water, using the data collected in Table 1 (the difference between the total mass in the two columns). After three weeks all the preparations were ready, but we verified a much faster growth for ADP (sometimes two or three days). This compound nucleates at lower concentration than KDP. In order to avoid the formation of many small crystals, the upper limit of concentrations given in Table 2 shouldn't be exceeded. It was not necessary to refrigerate the solutions, as the room temperature went below 7-9 ºC [2]. The best crystals were obtained from the lower concentrations (37g/100ml water). For comparative purposes, parallel experiments without any host or seed were performed using similar conditions. The crystals obtained were considerably smaller, and the most frequent habits were prismatic tabular (D) or squat prisms. We also found changes of habit depending on the purity of the solutions used: needles C were obtained with lower purity reagents, due to the presence of impurities in the bulk sample.

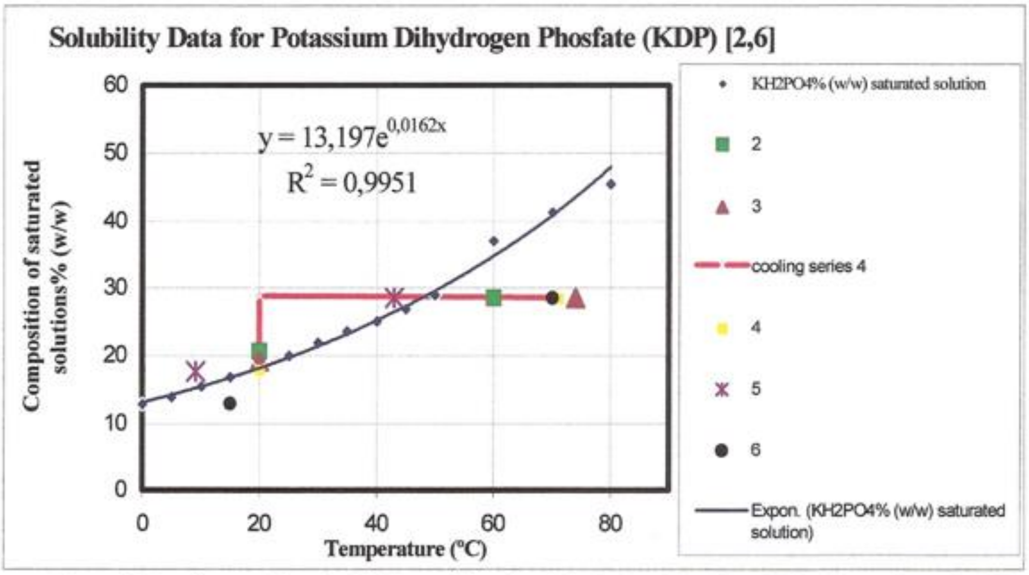


Figure 3-Experimental data for KDP crystallization "On the Rocks". The red line shows the period of cooling/ decrease on concentration arising from the crystal growth process.

The modifications of habit discussed above were detected using some of the hosts listed in Box 2, for the pure solutions of both compounds (Table 3, Figs. 1, 2). Inert hosts like glass and quartz don't react with these solutions and very pure single crystals A, either alone or in clusters are usually formed. Habits B and C occasionally coexist, most probably due to inclusions of iron compounds at the surface of quartz rocks. The major components of volcanic rocks are pyroxene (Fe, Mg, Ca silicates), olivine (Fe, Mg silicates), plagioclase (feldspar) and other minerals such as magnetite and biotite. As expected, all these rocks act as habit modifiers, producing beautiful long needles or whiskers C! Calcium carbonate from shells, limestone, marble and sedimentary rocks will react with the acid solutions (reaction 1), producing bubbling of carbon dioxide and increasing slightly the pH. As expected form A was frequently observed. Finally, we have no theoretical explanation why granite strongly stimulates crystal growth. B or prismatic forms are commonly observed in this case (Fig. 4).

$$CaCO_3(s) + 2H_3O^+(aq) \rightarrow Ca^{2+}(aq) + CO_2(g/l)\uparrow + 3H_2O(l) \quad (1)$$

Table 2-Some properties and main uses of ADP and KDP [2,6]

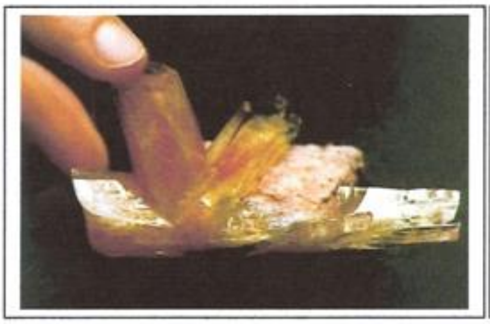
Compounds	**ADP** **Ammonium dihydrogen phosphate**	**KDP** **Potassium dihydrogen phosphate**
Common trade names	MAP monoammonium phosphate ammonium phosphate monobasic ammonium acid phosphate ammonium biphosphate ammonium phosphate primary	Potassium phosphate monobasic, MKP, potassium acid phosphate, potassium diphosphate, potassium orthophosphate
Some uses	Flame proofing agent, prevention of afterglow in matches, fertilizers, plant nutrient, food additive, manufacture of yeast, vinegar, yeast foods and bread improvers, chemical analysis, components for optoelectronics	Baking powder, nutrient solutions, yeast foods, buffer for pharmaceutical preparations and sequestrant, laboratory reagent, reference for non linear optics(duplicates frequency of radiation)
Colour	Brilliant white crystals or powder, transparent giant crystals, similar to quartz when distorted	Colourless crystals similar to ADP, translucent crystals
Crystal System **Common habits**	Tetragonal squat prisms, needles, etc. (Figs.1,2)	Tetragonal, similar to ADP
Vickers Hardness	69 (100) 3 (110)	150
Toxicity	No data	No data
Refractive index	1.5246	
Thermal stability;	Slightly hygroscopic	Slightly hygroscopic
Melting point /°C;		253
Density	1.803	2.338
Enthalpy of solution at infinite dilution/ kcalmol^{-1}	3.86 (room temperature)	4.5 (room temperature)
Synthesis	Reaction of phosphoric acid with ammonia	Reaction of phosphoric acid with potassium carbonate
Solubility, pH of aqueous solutions	0.2 M, pH= 4.2; Slightly soluble in ethanol; insoluble in acetone	Insoluble in ethanol , soluble in water, pH 4.5
Composition for crystal growth	37-42 g/100ml water The rock acts as habit modifier	37-52 g/100ml water The rock acts as habit modifier

Inclusion/occlusion of food dyes in ADP crystals

Giant crystals of inorganic metal complexes [1-4] can be extremely attractive for their wonderful colours, but they present some problems of toxicity and should be avoided or handled with care by young students. Fortunately ADP crystals can be doped by inclusion/occlusion of food dyes and other colorants (Tables 4, 5) with spectacular results, changing their colour, habit (Fig.4) and eventually their crystal system. This last approach is being exploited commercially in kits for crystal growing, and since 1995 these also contain pieces of granite to stimulate crystal growth, confirming our previous results for the pure compounds. Our attempts to colour KDP crystals were unfruitful (only tartrazine was tested). Data obtained for ADP are condensed in Table 5. Saturated stock solutions of each dye (SS) were first prepared from warm distilled water (60-70°C). The solutions were stirred to reduce the precipitation of the dye from the solution, during the cooling period of growth (*e.g.* 1g of dye powder per 100 ml of water). Pure ADP (*e.g.* 37.5 g) was then dissolved in 100 ml of this solution. From here on the preparation followed the general method described. The most attractive experiments are indicated in shadowed cells.

Table 3- Results of crystal growth for pure ADP and KDP

Compound	Mass of solute/g per 100g of water	Host	Crystal habit
ADP and KDP	37; 40		Squat prisms, tabular habits D, granular
ADP and KDP	>45 (ADP); > 55(KDP)		Nucleation, many small granular crystals
ADP and KDP	**≤40**	**Quartz**	**Habit A, clusters of large crystals**
ADP and KDP	≤40	Quartz with inclusions	Habit A and needles C, clusters
ADP and KDP	**≤40**	**Granite**	**Habits A, B or prismatic**, very large, **enhances crystal growth**
ADP and KDP	≤40	Marble, arenites, oyster, murex shells	Habit A, seldom B, clusters of large crystals
ADP and KDP	**≤40**	**Volcanic rocks Basalt**	**Enhances crystal growth, habit C, clusters of long needles or whiskers**
ADP	**40, non controlled evaporation to dryness**	**Volcanic rocks Basalt**	**Very attractive dendrites or needles C, looking like trees**



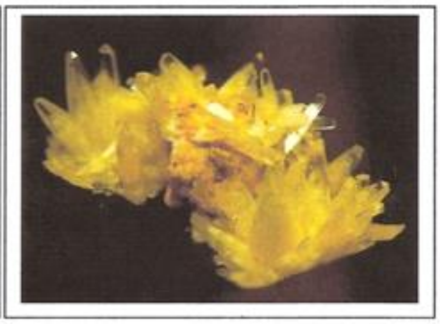


Figure 4-Left: Prismatic reddish crystals of ADP colored by Ponceau 4R. Right: (Reprinted from TEIXEIRA, C. (1999) Rochas Ornamentais e "Minerais Sintéticos", Brincando com a Cor. *Química, Boletim da Sociedade Portuguesa de Química,* 74, 55-58. Yellow crystals of ADP colored by

tartrazine; the habit is form B (tapered prism +pyramid) as represented in Figure 2. The inclusion of the dye is not uniform, decreasing towards the end of growth. Both samples were obtained using granite as host, stimulating crystal growth.

Table 4- Characterization of food dyes used for coloration of ADP crystals [8]

Food Dye, Formula	**[CAS] Color Index number**	**Some trade names**	**Properties. Color of dye. Other observations**
E102-**Tartrazine** $C_{16}H_9N_4\ Na_3O_9S_2$ (aromatic heterocyclic trisodium salt)	[1934-21-0] 19140	Food yellow 4, Acid yellow 23, Filter yellow	Bright yellow orange powder. Hygroscopic. Allergen. Incompatible with oxidizers[1].
E124-**Ponceau 4R** $C_{22}H_{20}O_{13}$ (carboxilic acid)	[1260-17-9] 75470	Cochineal Red A, Brilliant Scarlet 4R red, Carminic acid	Brown, dark red powder. Decomposes at 136ºC. Solubility: <0.1g/100ml water at 21 ºC. Soluble in ethanol, concentrated sulphuric acid. May cause irritation by short exposure. Incompatible with oxidizers [1]. Combustible.
E132- **Indigo Carmine** $C_{16}H_8N_2Na_2O_8S_2$ (disodium salt)	[860-22-0] 73015	Indigotine, acid blue W, Food Blue 2, Acid Blue 74	Dark blue-violet powder, crystals or granules. Light sensitive. Solubility in water: 1%. Slightly soluble in ethanol. May cause irritation by short exposure. Incompatible with oxidizers[1]. Moderately toxic by ingestion.
E110-**Sunset Yellow FCF** (disodium salt) $C_{16}H_{10}N_2\ Na_2O_7S_2$	[2783-94-0] 15985	Orange Yellow S, Food yellow 5	Slightly soluble in ethanol, 19% in water. Orange to red crystals. May cause irritation. Carcinogenic to animals. Incompatible with oxidizers[1] .
E122-**Carmoisine** $C_{20}H_{12}N_2\ Na_2O_7S_2$ (aromatic heterocyclic disodium salt)	[3567-69-9]	Azorubine, Acid red 14, Food red 5	Low solubility in water. Combustible. Reddish-brown powder.
E123-**Amaranth** $C_{20}H_{11}N_2\ Na_3O_{10}S_3$ (aromatic heterocyclic trisodium salt)	[915-67-3] 16185	Food red No 2, Bordeaus S, Acid red 27, Azorubine s.	Soluble in water, glycerin. Animal carcinogen. Purple red. Density 1.50.
E142-**Green S** $C_{27}H_{25}N_2NaO_7S_2$ (sodium salt)	[3087-16-9] 44090	Acid green 50, Wool Green S, Acid green BS	Purple to black powder. Light sensitive. A brilliant brown product is formed by decomposition of the dye. Soluble in water. Causes irritation. Incompatible with bases and oxidizers[1]. Moderately toxic by ingestion.
E133-**Brilliant Blue FCF** (Disodium salt) $C_{37}H_{34}N_2Na_2O_9S_3$	[3844-45-9] 42090	Food Blue 1, Acid blue 9, Erioglaucine	Soluble in water, ethanol. Causes irritation Allergen. Animal carcinogen. Slightly toxic by ingestion[1]. Purple to black powder.
Alizarin Red $C_{14}H_8NaO_7S$ (Sodium salt)	[130-22-3] 58005	Alizarin carmin, Sodium Alizarin-3-sulfonate	Soluble in water, slightly soluble in ethanol. Incompatible with oxidizers[1]. Allergen, causes severe irritation.

[1] Slight fire hazard. Dust/air mixtures may ignite or explode.

Final remarks

All dyes were effective coloring ADP crystals, by inclusion and occlusion simultaneously. Precipitation of the dye is almost always present, coloring the hosts and producing less brilliant crystals. Except for **Ponceau 4R,** the inclusions seem to produce a certain homogeneity of

Table 5- Results for successful inclusion/occlusion of food dyes in ADP crystals

Dye /Composition of Stock solution	Concentration of ADP/g in 100 ml Stock Solution SS	Host	Crystal habit, Other properties of crystals
Tartrazine SS ≈ 1g/100ml water. Very soluble dye. The solution is orange. Inclusions are producing a homogeneous **bright yellow to orange** coloration. An exception is shown in Fig.4, where inclusions are stronger in the beginning, when the GS is larger. Sometimes crystals become opaque. Occlusions also occur, producing less brilliant crystals.	35.7, 42.9		Clusters of tabular D, granular and large, subhedral and anhedral.
	53.1		Many small D or anhedral granular crystals.
	35.7	Granite, basalt, oyster shell	No crystals formed. Fortuitous!! The solution should have been refrigerated!
	35.7	Marble	One tabular D euhedric light yellow crystal.
	42.9	Shells and marble	Clusters of subhedral crystals with occlusion of the dye between faces.
	42.9	**Granite**	**B (Fig.4) or prismatic, very large, sometimes opaque yellow to orange.**
	42.9	**Basalt**	**Needles C; occlusion of dye between transparent and colored yellow needles.**
	40- non controlled evaporation till dryness	**Basalt**	**Very attractive dendrites or needles C, looking like bright orange trees.**
Indigo Carmine SS ≈ 1g/100ml water.	40 evaporation of solvent and cooling		Tabular D, granular and subhedral. Over them, **clusters of very large A crystals of a faint blue-violet almost homogeneous color.** Veils of growth. (one month growth).
SS ≈ 0.3 g/100ml water **Very faint and homogeneous violet-blue crystals are formed** by inclusion. Occlusion also occurs, increasing the coloration. The host is deep colored.	37.5, 45		Many tabular D and granular blue-violet crystals (14 days of growth).
	37.5, 45	**Basalt, volcanic rocks**	Wonderful clusters of blue-violet thin needles C (7 days of growth).
	37.5	**Granite**	**One large prismatic crystal.** Tabular and prismatic crystals out of the host (28 days of growth).
	45	**Granite**	**Large prismatic crystals. Enhances crystal growth** (7 days of growth).
Ponceau 4R SS ≈ 1g/100ml water. **The hosts are red deep colored. Non homogeneous red inclusions and occlusions occur.**	35.7		Clusters of granular D, red crystals (»15 days).
	42.8		One large crystal, Hopper growth (15 days).
	53.1		Clusters of euhedric crystals with occlusion of the dye (3 days).
	37.5	Oyster shells and marble	A, B, D large crystals with spots of dye (13 days). Hosts deeply coloured.
	37.5	**Granite**	**Large, prismatic, heterogeneous red color.** (7 days) as in Fig. 4. **Large prismatic tabular with red spots or veils.**
	37.5	Basalt	No crystals formed –fortuitous!
	45	Granite	Clusters, anhedric, strong red (3 days).
	45	Oyster shells and marble	Clusters, anhedric and subhedric strong red (7 days).
	45	**Basalt**	**Needles C. Occlusion between needles.**

Amaranth SS ≈ 0.3 g/100ml water.	37.5, 45		Granular D purple crystals.
	37.5, 45	**Basalt Volcanic**	**Large purple needles C.**
	37.5, 45	**Granite**	**Large purple prismatic crystals.**

Alizarin SS ≈ 1g/100ml water.	**40**	**Arenites**	**Light Pink-violet A large crystals. Occlusion and inclusion occur.**

Sunset Yellow SS ≈ 0.3 g/100ml water. **Strong orange coloration by inclusion (homogeneous)**/occlusion. **The crystallization starts immediately. The dye may act as habit modifier and also accelerate the growth.**	37.5, 45		**D granular orange crystals** (7 days of growth).
	37.5	**Basalt Volcanic**	**Very large, tabular, cross section B, orange crystal** (7 days of growth).
	45	**Basalt Volcanic**	**Very large D orange crystal covering the host** (7 days of growth).
	37.5	Granite	**Clusters D orange**
	45	Granite	**Very small D orange crystals**

Brilliant Blue FCF	37.5		Large D, brilliant (7 days of growth).
	45		Many granular D blue crystals.
SS ≈ 0.3 g/100ml water. **Intense blue crystals** by inclusion. Occlusion also occurs. Crystals are less brilliant after some days. The dye may act as habit modifier, favoring the X,Y growth (tabular).	**37.5**	**Basalt Volcanic**	**Large crystals (2), transition from C to B** (7 days of growth).
	45	**Basalt Volcanic**	**Needles transition from C to B** (21 days of growth). Less brilliant.
	37.5	Granite Large piece a) Small piece b)	a) Large tabular crystal, showing the top of the pyramid b) Tabular crystals (7 days of growth).
	45	Granite Large piece a) Small piece b)	a) and b) Tabular crystals (7 days of growth).

Carmoisine	37.5		Clusters of D (13 days).
SS ≈ 1g/100ml water.. Flocculates at 70°C or by addition of ADP. Strong precipitation of the dye, coloring the host. Reddish-brown crystals, with inclusions (homogeneous coloration, pink) but stronger occlusion.	37.5	Marble	Clusters, anhedric.
	37.5	Oyster Shells	Tabular clusters subhedral.
	37.5	**Basalt**	**Needles C with occlusion in between.**
	37.5	**Granite**	**D, Prismatic, pink.**
	45	Oyster Shells	A and anhedric.
	45	Marble	D
	45	**Basalt**	**Needles C, pink.**
	45	**Granite**	**Clusters of Large B, like quartz.**
SS ≈ 0.2 g/100ml water Less flocculation. Pink crystals by inclusion and occlusion.	**45**	**Basalt**	**Clusters of A, B almost transparent crystals on a colored host.**
	45	Marble	A, large, some tabular, slightly pink. Deeper coloration in the pyramid.
	45	Granite	A, large, slightly pink.
	45	Oyster shell	Clusters A, stronger coloration in the pyramid

Green S SS ≈ 0.3 g/100ml water. Blue solutions. Decomposition of the dye occurs: a brilliant	37.5		**Granular D** (21 days of growth).
	45		One anhedral crystal (7 days of growth).
	37.5	**Basalt**	**C transition to B very large blue crystals** (7 days of growth).

brown powder in suspension and covering all the hosts used is formed. The starting material used to prepare SS was already decomposed. All crystals are **light blue.**	**45**	**Basalt**	**B very large blue crystals** (7 days of growth).
	37.5	**Granite**	One large and one smaller prismatic blue crystal (7 days of growth).
	45	Granite	One anhedral blue crystal covering the host completely (7 days of growth).

50% tartrazine+ 50% Brilliant Blue FCF SS ≈ 0.3 g/100ml water. Green crystals, with inclusion and occlusion.	37.5, 45		Green tabular large crystal, hexagonal cross section (15 days of growth).
	37.5	**Basalt**	**Needles C to B, large on the host** and small outside the host (15 days of growth).
	45	Basalt	Large anhedric crystal.
	37.5	Granite	No crystals formed.
	45	Granite	Very large covering the host with hexagonal cross section (15 days of growth).

colour. This fact may be related to its chemical composition, a carboxylic acid unlike the others, all of them sodium salts. Basalt and granite induce even faster crystal growth compared to marble and oyster shells. Tartrazine doped crystals were systematically studied and behave much like the pure samples of ADP in the presence of the several hosts. The other results should be regarded as preliminary, and further research has to be done, possibly controlling the temperature, rate of cooling and evaporation, to get reproducible data and avoid random results. In our opinion, basalt and volcanic rocks are producing the best and safer results. Most of the samples prepared are very attractive, though. Finally, do not forget the general safety rules given below [8], and always prepare a stock solution of the food dye to decrease its toxicity, especially when primary schools are involved in this project:

Always wear a lab coat, goggles, and gloves. If toxic substances are used prepare the solutions in a fume hood. If not available (depending on the toxicity of the substances) work in a well ventilated room and wear at least a powder mask for grind up the solid substances. Avoid breathing the vapors [8]. Note that the use of toxic substances for demonstrations should be avoided.

Appendix

Table 6 –Solubility Data of ADP and KDP [2, 6]

T/°C	Solubility $(NH_4)H_2PO_4$ g/100g water	Solubility KH_2PO_4 g/100g water	Solubility KH_2PO_4 mass% saturated solution	Density of ADP saturated aqueous solutions	Density of KDP saturated aqueous solutions
0	22.0	15.9	12.88	1.13	1.11
5			14.00		
10	28	18.3	15.50	1.14	1.12
15			16.87		
20	36.5	22.6	18.45	1.16	1.15
25			20.04		

30	45.8	27.7	21.90	1.18	1.17
35			23.65		
40	56.6	33.5	25.10	1.21	1.20
45			26.90		
50			29.00	1.24	1.23
60		50.0	37.05	1.27	1.26
70			41.30	1.30	1.31
80		70.4	45.50		

Table 7-Densities of aqueous solutions at 20ºC [2, 8]

Mass %	1	2	3	4	5	10	12	14	16	18	20	22	24
ADP	1.006	1.012	1.018	1.023	1.029	1.058	1.070	1.081	1.093	1.104	1.115	1.128	1.141
KDP	1.007	1.014	1.022	1.029	1.036	1.072							

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