

Cyanotype: an artistic way to talk about (photo) chemistry

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Abstract

The present manuscript describes the well know cyanotype process and how it can be intuitive, easy and, low cost photochemistry experiment. We discuss basic laboratorial techniques, syntheses, dissolutions, chemical reactions, and preparation of solutions to undergraduate students, especially to begging students. Besides the common laboratory routines, some concepts like stoichiometric calculations, concentration units, photochemistry reactions, and coordination chemistry also are discussed. In addition, we propose some adaptations of photochemistry experience using common laboratory materials and fitting the whole experiment in two hours. Undergraduate students will have the opportunity to prepare a photosensitive paper as well to achieve remarkable photographic images, due to the formation of the *Prussian blue* pigment, making the class more playful, stimulating creativity and making the learning environment unique.

Keywords: Cyanotype, First-Year Undergraduate, Laboratory Class, Photochemistry,

1. Introduction

Chemical photographic processes have been known since the mid-19th century, and continuous modifications throughout decades have improved methods for photographers. Among of photographic processes, the cyanotype technique, reported by scientist Sir John Frederick William Herschel in early 1840s, has been used for engineers, architects, draftsmen and other workers to make blueprint copies since 1870s [1]. As well, the cyanotype technique has been popular for artists and artisans where extensive collections of blue images of a number of materials have been reported [2]. The success of cyanotype printing, perhaps is

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due to its chemical compounds and process, it means, the relatively nontoxic materials, stable product, low cost and easy to use its chemical reactants.

On the other hand, the cyanotype is an interesting laboratorial experiment to explain chemistry, especially, photochemistry and coordination compounds to undergraduate students. Several works have been discussed cyanotype process as a vehicle to introduce chemical principles to students of beginning science courses [2-9]. Usually, the cyanotype experience has been shown to students theoretically or just as demonstration, since the cyanotype process has sensitive photographic materials that take time to be done and should be far away from UV radiation or sunlight [7-9]. However, the solutions can be properly prepared and used in the common chemical laboratories, and with few adaptations, the cyanotype process, it means, solution preparations, painting paper, light exposition, washing material and so on, can be done in two hours, which is usually time of laboratory undergraduate classes. There is one-step missing to complete the whole cyanotype process – the light sensitive paper, which is prepared unless one day before of the undergraduate experience.

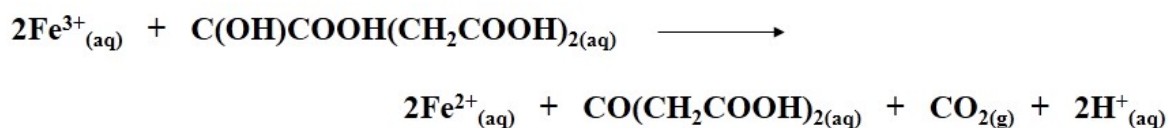
Briefly, the former process of cyanotype consists in a sensitized paper an aqueous mixture of ferric ammonium citrate and potassium ferricyanide. The Fe^{3+} ions became Fe^{2+} ions after sunlight or UV light exposition with citrate ions as electrons donor. The Fe^{2+} ions in solution with ferricyanide ion and subsequent *inner-sphere* electron transfer, forms poor soluble ferric ferrocyanide-iron (III) hexacyanoferrate (II) in aqueous solution, or *Prussian blue*. The intense blue color of the *Prussian blue* is due to the mixed oxidation states of iron ions and its zeolite character [2]. The chemical formula of poor soluble *Prussian blue* is $\text{Fe}_4[\text{Fe}^{\text{II}}(\text{CN})_6]_3 \cdot x\text{H}_2\text{O}$, where $x = 14$ to 16 and its crystal structure was solved and determined by W.HALG in 1980 using both X-ray and neutron measurements as well IR and Mössbauer spectroscopies have been reported to support the reported structure [10].

After sufficient exposure to UV light, the paper should be washed in water to remove the soluble unexposed salts. Upon drying, the final image darkens as a result of either slow oxidation in air or some changes in iron coordination with loss of water [11].

Few years ago, in 1994, Mike Ware proposed to use ammonium tris(oxalato)ferrate(III) instead of iron(III) citrate, since iron oxalate complex is more sensitive to sunlight or UV light than citrate iron salt [11].

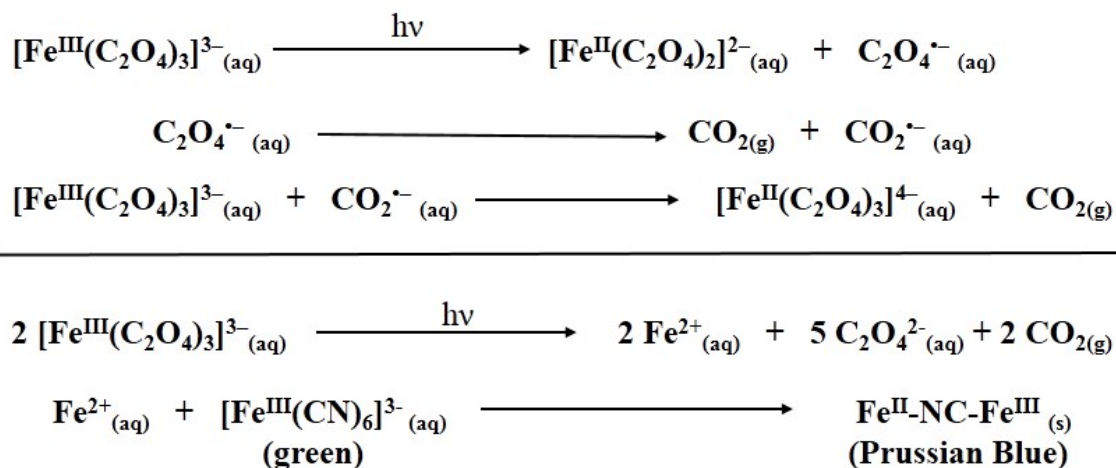
The oxalate iron salt also have been widely used as actinometer due to its high light sensitivity [12], as well the photochemical reaction of ammonium tris-(oxalato)ferrate(III) is faster than citrate one [11], also the oxalate aqueous solution can be stored as it does not affected by fungi [11]. The chemical composition of ammonium citrate iron is not well defined but both oxalate and citrate iron salts have its photochemical reaction mechanisms well elucidated. The photochemical mechanism for citrate iron is depicted in the scheme 1 [2]. The products of photooxidation of coordinated iron citrate are initially carbon dioxide, CO₂ and acetone dicarboxylate, which thermally decarboxylate generating acetone molecule as the final organic product. The photochemical reactions of cyanotype reactants are pH dependent, where the optimum pH condition for best quantum yields, nearly 0.45, is into the pH 2-5 range.

Scheme 1: Proposed photochemistry mechanism of iron citrate. The spontaneous decarboxylation of acetone dicarboxylate compound has not been represented.



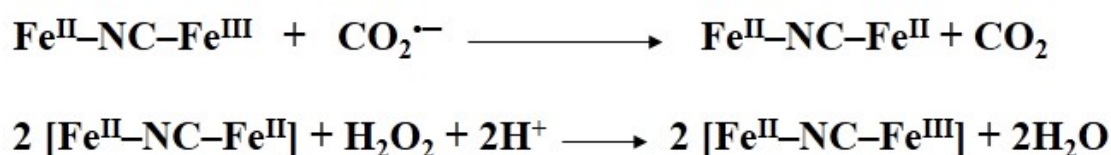
The photochemical mechanism of oxalate iron solution is described in the scheme 2 [1]. Initially, the Fe(III) ion reduces to Fe(II) under radiation (light) and radical oxalate is formed. Subsequently, the radical oxalate degrades into a carbon dioxide molecule and another species, the radical carbon dioxide. The CO₂^{•-} reacts with the other ion [Fe^{III}(C₂O₄)₃]³⁻ to form Fe(II) and C₂O₄²⁻ ions and CO₂ as gas. The Fe(III) ions that have been reduced to Fe(II) react with the ferricyanide ion and after *inner-sphere* electron transfer, the *Prussian blue* or Fe₄[Fe^{II}(CN)₆]₃·xH₂O precipitates as a cyanide complex that contains both Fe(III) and Fe(II) ions.

Scheme 2. Proposed mechanism of photodecomposition of iron oxalate.



If an overexposure to light occurs, excess $\text{CO}_2^{\bullet-}$ can be formed, and consequently it can promote the reduction of counter ion Fe^{3+} to Fe^{2+} , as depicted in the scheme 3 [13]. When the counter ion is Fe^{2+} instead Fe^{3+} , the *Prussian Blue* become "*Prussian white*", it means, the final color is white instead blue. In this case, only a pale image arises. However, it can be avoided or reversed by the oxidation of the $\text{Fe}(\text{II})$ ion back to $\text{Fe}(\text{III})$, dipping exposing images into a solution of hydrogen peroxide. An alternative way to turn pale to blue images is just waiting for the molecular oxygen present in the air to promoting oxidation of iron(II) to iron(III) ions. However, from a photographic point of view, bathing with H_2O_2 is more artistic and faster than atmospheric oxygen.

Scheme 3. Sequence of reactions to recovery light overexposed *Prussian blue* photo



Despite the advantages of oxalate iron solution over citrate iron solution, the solubility of the ferric oxalate ion depends on the counter ion. In the presence of potassium ions the oxalate iron complex precipitates in aqueous solution as potassium ferric oxalate [14]. In the presence of the ammonium ions, the compound formed by ammoniacal ferric oxalate remains soluble in the aqueous medium. However, it well known in the cyanotype process that the potassium ferricyanide is widely used. Potassium ferric oxalate as precipitate may interfere the photochemical outcome [11], since it reduces the photosensitivity of the mixture, requiring a long time of exposure to light.

Fiorito and Polo, in 2015 [7], describe a feasible routine of cyanotype process for conventional undergraduate chemical laboratories, using the Iron(II,III) hexacyanoferrate (II,III) or simply known as *Prussian blue* salt and potassium tris-oxalatoferate(III). The experiment described by Fiorito and Polo has been dedicated to chemistry students and conducted in two or three laboratory sessions of 2 hours each.

The current paper presents an experiment fitted about 2 hours that has been used in the experimental subject of beginning students of chemistry laboratory at UFJF. The experimental section describes the solution preparations, routine and common materials current in chemical laboratories. It is worth noting that the undergraduate students are from different areas of exact sciences like engineers, physics, chemists, mathematics, statistics, and so on. Also, the current experimental class will be implemented in the laboratory coordination chemistry course soon.

2. Experimental

Solution preparations

Step A) Synthesis of the $(\text{NH}_4)_3[\text{Fe}(\text{C}_2\text{O}_4)_3]\cdot 3\text{H}_2\text{O}$ complex

- a1) Weight 5 mmol of ammonium oxalate, in excess [16];
- a2) Dissolve the $(\text{NH}_4)_2\text{C}_2\text{O}_4$ in 5 mL of water about 50°C;
- a3) Weight 1.6 mmol of $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$;
- a4) Add $\text{FeCl}_3\cdot 6\text{H}_2\text{O}_{(s)}$ to the ammonium oxalate solution and stirring it for about 15 minutes;

Step B) Preparation of the photosensitive solution

- b1) Add 0.5 mL of 3% $\text{K}_3[\text{Fe}(\text{CN})_6]$ solution to the previously prepared ammonium tris(oxalato)ferrate(III) solution;
- b2) Mix the two solutions until to obtain a homogeneous color solution.

Step C) Impregnation of the photosensitive solution on the filter paper

- c1) with a brush, paint a paper uniformly with the solution prepared in item b2;
- c2) place the paper still humid in the oven at 50°C and dry it for about 10 minutes;
- c3) prepare your drawing (or object) to be used to 'develop' the photo.

Step D) Preparation of the photo

- d1) Take the impregnated and dried paper and place it on the glass;

- d2) Place your drawing or object over the paper; if necessary, place another glass over the drawing/object;
- d3) Expose the prepared material to sunlight or under UV light for the photochemical reaction to take place; leave it about the light for 10 minutes;
- d4) Dip for 10s the paper in the bath containing 0.3% hydrogen peroxide;
- d5) Dry the set, take it home and enjoy your art.

Photographic procedure

Some objects like keys, jewelry, flowers, leaves, and so on can be placed on the photosensitive paper to obtain the blue photo. An alternative is to print negative images in black and white using transparency pages. The object or transparency should be placed over the photosensitive paper and the set exposed to light. In the case using transparency, leaves, flowers and anything like that, it is better to be placed on the paper and under a glass plate (Figure 1). The set should be exposed to the sun or UV lamp. Usually, about 10 minutes over the sun or UV lamp is enough to promote the photochemistry reaction. However, may be the photochemistry take a little longer, about 20 minutes, when using the sun as source of energy, especially in cloudy days.



Figure 1. Final images of leaves and transparency placed over photosensitive papers after exposed to UV light.

UV lamps can be used, and the exposure time can be estimated. After the light exposure, the paper with the formed image should be washed with water to remove the photosensitive mixture that was still present on the paper. Figure 2.



Figure 2. Remarkable image obtained using the proposed experiment

Complementary experiment

Iron(III)-SCN test: In a test tube, add a few drops of ammoniacal ferric citrate solution and in the other test tube put a few drops of the ammoniacal ferric oxalate solution synthesized in the experimental class. Drop of potassium thiocyanate aqueous solution $[0,1, \text{mol.L}^{-1}]$ and changes in the solution color can be noted on Figure 3. Briefly, thiocyanate– $\text{SCN}^-_{(\text{aq})}$ ions react with iron(III) ones in aqueous solution. The equilibrium mixture of $\text{Fe}^{3+}_{(\text{aq})}$, $\text{SCN}^-_{(\text{aq})}$ and $[\text{FeNCS}]^{2+}$ species are formed, as described in the equation 1.



In neutral to slightly acidic solutions, the $\text{Fe}^{3+}_{(\text{aq})}$ ions are very light yellow color in aqueous solution and the $\text{SCN}^-_{(\text{aq})}$ ions are colorless. However, the ion complex – $[\text{FeNCS}]^{2+}_{(\text{aq})}$ presents intense blood red color in solution. So, the free $\text{Fe}^{3+}_{(\text{aq})}$ could be easily detected with thiocyanate ions since the final solution became dark red [15].

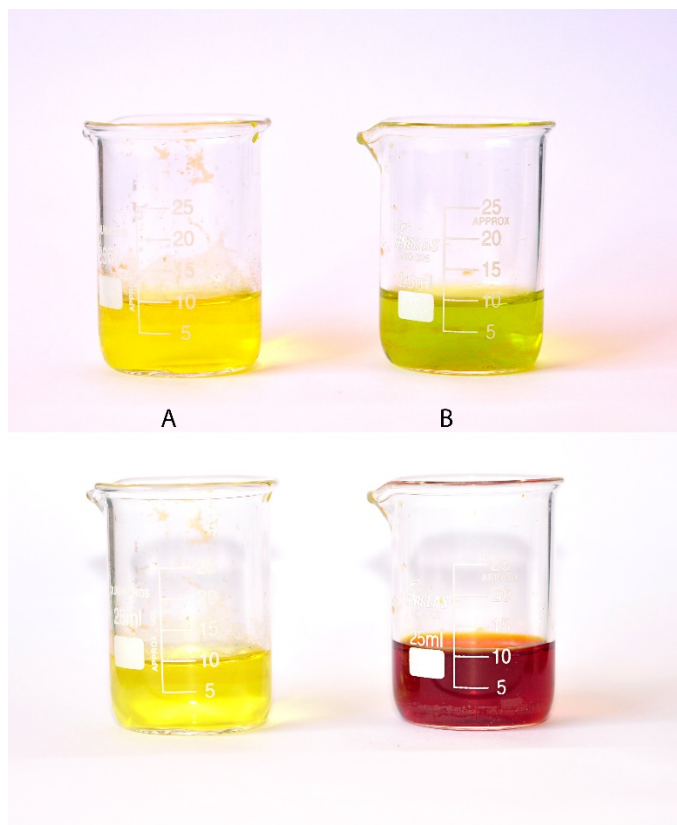


Figure 3. Iron(III)-SCN test: (A) solution of commercial ammonium ferric citrate before (top) and after the test (bottom); (B) solution of ammonium tris-(oxalato)ferrate(III) before (top) and after the test (bottom).

3. Final remarks

During and after the cyanotype processes it is possible to discuss some concepts involving light as source for photochemical reactions. In about 2 hours, as long as the class, several discussions with students should be done to assess their knowledge of the cyanotype experiment that takes place to obtain amazing blue images.

The main objective of an experimental science course for beginners is to introduce students to important chemical principles, and in this case, using an experiment that provides the pleasure and excitement of experimental chemistry. In addition to touching curiosity, since the outcomes of cyanotype experiment could be sometimes amazing images.

This manuscript brings the use of warm *in situ* ammoniacal ferric oxalate to prevent the precipitation of potassium ferric oxalate. The previous synthesis already published brings potassium ferric oxalate or even ammonium oxalate, a number of steps to obtain the compound, a number of reagents and adjustments in the solutions to perform the cyanotype process [7,11,16]. In the present work, the steps, adjustments and reagents have been reduced, saving time and without harming the process and the contents to be covered in class.

The use of laboratory filter paper instead of watercolor paper brought the advantage of having a water resistant paper already available in the laboratory. Regarding drying, watercolor papers are normally expected to dry for 1 day, which would prevent the class from being held in a 2 hours class. An alternative would be the use of hair dryers, which are not always available in common chemical laboratory. The proposed alternative, which is the use of a stove previously warmed at 50 °C, that allows the several filter papers to be dried simultaneously, attending many students at once. Stove drying occurs relatively quickly and the compounds used in the photosensitive mixture are stable at the chosen temperature [17, 18].

The photochemistry reaction could not occur completely to form the complex $(\text{NH}_4)_3[\text{Fe}(\text{C}_2\text{O}_4)_3]\cdot 3\text{H}_2\text{O}$, which is the photosensitive compound, and the Iron salt used in the synthesis, perhaps, still as free $\text{Fe}^{3+}_{(\text{aq})}$. The free Fe^{3+} ions in aqueous solution can be detected using SCN^- ions, since it forms the ion $[\text{FeNCS}]^{2+}$, a ion complex with an intense bloodred color. Using the thiocyanate in the commercial solution of ammoniacal ferric citrate, no reddish solution is formed since no free $\text{Fe}^{3+}_{(\text{aq})}$ ions are available. Perhaps Fe^{3+} ions are complexed by the citrate ions. This discussion is interesting because it highlights the importance of the purification and isolation steps of compound obtained in the synthesis, which in the case of this work did not occur.

The proposed script can also be applied to the experimental discipline of coordination chemistry, just adjusting the discussions. If the teacher chooses to use the present script in coordination chemistry, the synthesis of the potassium or ammonium ferric oxalate compound can be performed as well, and the differences in the synthesis as well the solubility can be discussed. As described in Scheme 2, there is an electron transfer reactions that occur *via* covalent bond $\text{Fe}^{\text{III}}-\text{CN}-\text{Fe}^{\text{II}}$, and *inner-sphere* mechanisms in Octahedral complexes can be also discussed with Coordination Chemistry students. Another topic is the electronic spectrum interpretation using the molecular orbitals diagrams [19] since the UV-Vis absorption spectroscopy can be used.

The “thiocyanate” test in coordination chemistry can lead to the discussion of kinetic and steric effects in obtaining the compound with the oxalate ligand. Since the SCN^- is an ambidentate ligand, topics as HSAB (hard and soft acids and bases) nomenclature of inorganic complexes can be also discussed with students.

The experiments are safe, the procedures do not require special care and the rejects are easy to dispose of. However, the use of protective equipment is always highly recommended.

Finally, Cyanotype experiment is a feasible photochemistry experience to be applied to basic laboratory (for begging students) or for coordination chemistry since several concepts on laboratorial routines, general chemistry and inorganic chemistry can be discussed.

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