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Introducing the *Human Element* in Chemistry by Synthesizing Blue Pigments and Creating Cyanotypes in a First-Year Chemistry Course

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ABSTRACT: In this article, we present two concrete applications of the concept of the *human element* to chemistry education; starting with a course and experimental project on blue pigment synthesis and concluding with cross-disciplinary lessons and experiments on blue photography. In addition to the description of the content of these courses, we explore the motives that led us to taking this approach, its place in the local academic context, and the first results of these pedagogical experiments.

KEYWORDS: *First-Year Undergraduate/General, Interdisciplinary/Multidisciplinary, Dyes/Pigments, Hands-On Learning/Manipulatives, Inquiry-Based/Discovery Learning*

■ INTRODUCTION

During the first academic year, chemistry courses are very important because students have to acquire the basic notions of the field. As such, students are faced with major difficulties. Among those stand the omnipresent and implicit changes between the macroscopic, submicroscopic and symbolic levels. The macroscopic level is employed when one talks of chemical characteristics that are directly accessible to our senses, like colors. Then one arrives at the submicroscopic level when describing matter and transformation at the scale of atoms and molecules. Finally, one jumps to the symbolic level in order to represent reactions and elements in a concise and formal way, using symbols and mathematics. Identifying those three levels and connecting them is neither obvious nor automatic for students, although this process is a necessary condition to understand chemistry thoroughly. The "triangle of thinking level", developed by Johnstone and Gabel,[1,2] has sharpened our vision of the interaction of the three levels and helped us to be aware of all three levels of understanding, rather than working almost exclusively at the symbolic level. The triangle metaphor reminds us of the importance of balance between the symbolic and the macroscopic levels and between theorizing and describing as activities emphasized in university courses.

Students' interest in studying chemistry steadily decreasing in the last few decades, the authors of this paper have been looking for ways to render chemistry an attractive subject. But does the triangle of thinking levels offer us an appropriate solution to the educational challenges we must face to motivate young people to continue studying chemistry and to rebuild trust with the public? Mahaffy answers negatively to this question and maintains that educators need to add one further dimension to their teaching of chemistry. He proposed to extend the triangle of learning levels to form a tetrahedron, where the fourth vertex represents the web of human contexts in which chemistry has evolved: *the human element*.[3] According to Mahaffy, tetrahedral chemistry education can serve as a metaphor for describing what we value in chemistry education by situating chemical concepts, symbolic representations, and chemical substances in the authentic contexts of the human beings who create substances, the culture that uses them, and the students who try to understand them.

Convinced by the argument that the human element brings a whole new dimension into the understanding of chemistry, we decided to develop it in two different ways in our courses:

- Cross-disciplinarity: Our understanding of the chemical concepts and reactions is informed by the rich web of sciences, history and the arts (painting and photography).
- The human learner: Our chemistry education emphasizes investigative laboratory projects.

This paper presents blue pigment synthesis and blue photography experiments. Such teaching can follow the interplay between chemistry and the visual arts. Articles on chemistry and art were numerous in this *Journal*.[4,5] And we are convinced that it is worth keeping on insisting on the rich relationship between chemistry and art, as it may lead to important changes of our teaching.

■ CONTEXT

Before coming to the core of our courses and their connections to the theories developed by Johnstone, Gabel and Mahaffy, it is necessary to first describe the context in which they take place. It is also important to note that the two pedagogical experiments we will describe later are just one element of a larger bachelors program that places emphasis on the *human element*. This course is being developed in a new and original bachelors program named *Sciences and Humanities* that began in September 2012 at the University of Aix-Marseille, France. This program is based on cross-disciplinarity and aims to prepare students to master a level of complexity of thinking as defined by the sociologist and philosopher Edgar Morin.[6] The idea is to bring students face to face with the diversity and complementarity of the answers proposed by each discipline to a complex problem. Therefore, one goal of this particular bachelors program is to train students to tackle questions in a global and comprehensive way. Another goal is to try to resolve the well-known dilemmas created by the modern disjunction of

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the different fields of knowledge.[7,8] The program is based on five wide and representative themes of work. These themes are called: (i) *Nature and Culture*; (ii) *Logic, Language, Computing*; (iii) *Systems of the World*; (iv) *Figures of Power*; and (v) *Optics, Vision, Color*. They were selected so that rich and complex thinking and understanding may arise from the confrontation of the diverse viewpoints given by the different disciplines regarding those themes. Indeed, each of these themes is related to several disciplines that all treat them with their own logic and coherence, imposed by their own inevitably reductionist approach to the world. The two experiments depicted in this article take place in the frame of the course *Optics, Vision, Color*. We decided to treat this theme by following a resolutely historical path. The first semester is dedicated to Antiquity and the Arabic Middle-Ages. It begins with a first reflection on the nature of Color, through a course on the synthesis of Egyptian blue as described in the following section of this paper. This course includes historical and chemical considerations on the development of blue pigments, as well as the viewpoint of artists on that color. In parallel to this course, students follow a series of lectures on the various theories of Optics, and more precisely of Vision, in Greek Antiquity and in the Arabic Middle-Ages. Since a deep understanding of the development of the theories of Optics cannot be disentangled from the development of Geometry, Arts (perspective of set pieces, painting, statuary), Philosophy, and Anatomy, students also study those topics. The second part of this article will describe how a course on photography was developed, based on chemistry, mathematics, physics, history, and the arts.[9] As one may see, these two examples will naturally interweave approaches that are relative to the natural sciences (chemistry, physics, mathematics and biology), the human sciences (history, psychology, philosophy) and the arts. They were first selected for this article because they are particularly representative of the new methods and models of teaching that we intend to develop in the *Sciences and Humanities* bachelors program. Second, they are presented in order to outline the introduction of the *human element* in our chemistry course.

■ SYNTHESIS OF EGYPTIAN BLUE PIGMENT

The blue color was chosen rather than any other because, if one digs into the history of colored pigments, it becomes clear that with a few rare exceptions (lapis lazuli, azurite), blue pigments are not available in nature and were all synthesized artificially by Man. Due to this, we thought that it would be relevant to highlight the ingenuity of those men who, driven by the strong aesthetic appeal of that color, synthesized the blue materials that were not directly available around them. In this sense, blue pigments can be considered as milestones in the history of chemistry. Therefore, the course is first focused on the historical and chemical study of the use of blue pigments (Egyptian blue, Azurite, Prussian blue, cobalt blue and ultramarine blue) in art. Consequently, this first course retraces the history of natural and synthetic blue pigments connecting together:

- the names, tints and formula of those pigments
- their detailed chemical synthesis and the historical and scientific context in which they were invented (handicraft in Egyptian antiquity, extraction from a natural blue stone in Italian Renaissance, Alchemy at beginning of the 18th century, Chemistry at the beginning of the 19th century, and Chemical engineering since 1828)
- the work and artistic approach of some of the painters who were using them (Giotto, Watteau, Van Gogh, Monet and Klein).

We insist on the fact that this course is strictly focused on blue pigments. The question of blue dyes, like indigo, is actually treated in a biochemistry course on the color of plants that takes place during the second year of the program.[10]

After this, students are gathered into groups of four in order to develop, without the assistance of the teacher, an experimental project. They are asked to set up an experimental protocol leading to the preparation of Egyptian blue ($CaCuSi_4O_{10}$) from silica (SiO_2), copper oxide (CuO), calcium carbonate ($CaCO_3$) and sodium carbonate (Na_2CO_3). Today, Egyptian blue is generally regarded as a multiphase material that was produced by heating quartz sand, a copper compound, calcium carbonate, and a small amount of an alkali at temperatures ranging between 800 and 1000 °C for several hours. The result is cuprorivaite or Egyptian blue and carbon dioxide as described by the following reaction

$$CuO + 4SiO_2 + CaCO_3 = CaCuSi_4O_{10} + CO_2 \qquad (1)$$

During these experimental projects, chemistry-teaching laboratories are open 3 to 4 h a day during a whole week. A teacher is present for safety reasons but is never involved in scientific matters at this stage of the process. Students here have to hypothesize, choose a question for further investigation, plan and conduct their experiments, and finally analyze their results (or absence of results) in order to come to a conclusion on the chemical mechanisms involved. Starting from bibliographical research, students have to explore empirically the importance of the experimental conditions (masses, temperatures, heating rates) on the color of the pigment. Here again, the idea is to work on the *human element* (in the sense of "human learner" this time) in order to use it as a connector between the three formal thinking levels of chemistry. Indeed, during this experimental project, students regularly have to connect together the macroscopic (color of the sample) and submicroscopic (chemical formula of the sample) levels. In addition, a connection with the symbolic level is made by studying the mechanism proposed in 1987 by G. Onoratini[11]

$$CaCO_3 = CaO + CO_2$$

$$\text{around 750 °C} \quad CaO + SiO_2 = CaSiO_3$$

$$\text{around 850 °C} \quad CaSiO_3 + CuO + 3SiO_2 = CaCuSi_4O_{10}$$

Besides this, students were brought to the Museum of Mediterranean Archeology in Marseilles in order to question the place of the blue color in Egyptian culture. We also went to the Museum of Modern Art and Contemporary Art in Nice where a visit is organized around Yves Klein's painting collection. Yves Klein was fascinated by ultramarine blue and he worked for five years with a chemist in order to develop the formula of a binder that would allow him to construct layers that would conserve the color of the untreated pigment. The International Klein Blue (IKB) formula was published in 1966. Finally, all the groups of students were asked to present their experimental results and how they can place these in the context of theories developed in the course and in literature.

What happened? All groups of students tried 2 or 3 different values for the masses of the products, for the final temperature of furnace and for its heating rate. And they all finally obtained samples of blue pigment as shown in Figure 1 which, when

Figure 1. Blue pigments as prepared and used for painting by students at the University of Aix-Marseilles, France, 2012. Reprinted with permission of Jean-Yves Briend (left image), Julia Astier (center), and Esther Miglio (right).

examined using X-ray diffraction (Figure 2), fell within the characteristics of Egyptian blue, which is already a positive

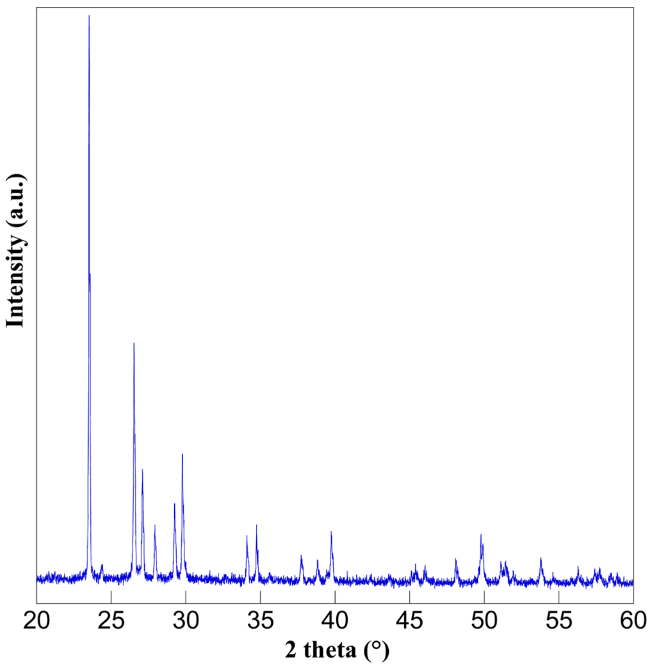

Figure 2. X-ray pattern of blue pigment prepared by students. (All peaks are typical to the cuprorivaite phase.)

result. It is important to note that students do not analyze the X-ray diffraction pattern during this course. It is the teacher who used it afterward in order to confirm the nature of the synthesized pigments. But X-ray diffraction pattern of the Egyptian blue is then studied during the second year of the program, as part of a course of physics focused on the consequences of Fresnel's works in the field of optics.

Another important outcome concerns the students' attitudes and interest in chemistry laboratory work.

Typically, in a classical chemistry laboratory, students are used to performing experiments in small groups (2–3 per group) by following the steps depicted in a laboratory manual, that is, students are asked to conduct experiments based on specific and explicit instructions. On the contrary, our pedagogical approach here is based on inquiry-type experience. As a result, we observed a greater degree of participation in the science laboratory, resulting in an improved attitude toward chemistry learning and toward practicing in the chemistry laboratory. Although our teaching objective was focused on experimental processes (hypothesis, experiment plan, experimentation, conclusion), the majority of students asked to perform an analysis of the fine structure of their final compounds.

Moreover, during the course, the instructor had mentioned Gerard Onoratini's work on Egyptian blue. And after the laboratory session, surprised by their own experimental results, students asked to meet him in order to clarify the role of the alkali and the role of the temperature on the Egyptian blue synthesis. The exchange was rich. Personal questions—we could qualify as *human* questions—related to the circumstances of the researcher's original work, his own tricks and methods, his inspirations were mixed to their scientific questions as they were trying to understand the motives of the 12 years-long work of the researcher on Egyptian Blue. One can easily imagine that students will develop a more complete understanding of what chemistry really is by listening to who chemists are. As mentioned above (second section), visual art also performs the role of the *human element* of our course through the historical study of the use of blue pigments. Note worthy is also the fact that students used their pigments for painting (Figure 1). We noted that this additional and personal motivation had a huge impact on their involvement in this laboratory work, to which they dedicated an amount of time and energy that was rarely seen in our classical chemistry laboratory studies.

Finally, we would like to stress the fact that during their presentations, most of the students exposed their experimental plan, argued the values they had chosen for masses, temperatures and heating rates from literature data, relied on Onoratini's mechanism to explain their different syntheses and proposed new experiments to complete their results. This behavior seems a type of evidence that the most basic objectives of this course on introductory chemistry were achieved. We also mention students usually introduced elements of the history, sociology, symbolism or artistic use of the blue color in order to explain their motivation behind their experimental work.

■ BLUE PHOTOGRAPHY EXPERIMENTS

Another example of our pedagogical cross-disciplinary method is developed within a course on photography merging the approaches of an artist, a mathematician, a physicist and a chemist. First, the course starts with a short introduction about the birth of photography, mainly based on the *short history of photography* by Benjamin.[12] The idea is to show how various and seemingly unrelated aspects can be intertwined when studying such a subject: art, science, politics and philosophy. Therefore, we wish not only to understand the chemical aspects of the Daguerian process, but also to address the following questions:

- Why was photography born at the beginning of the 19th century?
- What are the relationships between photography and art, especially painting?
- What is the whole idea behind photography?

Second, we attempt to have the students practice photography by using a large format camera, first used as a simple pinhole camera, in order to lead students to discover the basic concepts of projective geometry and more precisely of Desargues' theorem.

Third, we focus on the study of a photograph or a group of photographs. This year we have chosen to work on the Surrealists and on André Kertesz (Figure 3). Students took a few photographs in the spirit of this movement, making use of their theoretical knowledge of the geometry and the physics[13] of the pinhole camera.

Figure 3. Cyanotype of *Chez Mondrian* by André Kertesz (1926). Reprinted with permission of Jean-Yves Briend.

Finally, the course returns to chemistry. The silver-based chemistry of photography is very complex. We thus focus on the cyanotype printing principle, also known as blue print and first described by J. F. Herschel in 1842.[14]

As a result of this photographic experiment, we are able to work on a concrete illustration of oxidation−reduction reaction and on the catalytic effect of ultraviolet radiation on some chemical reactions. The photosensitive solution is prepared using potassium ferricyanide $K_3[Fe(CN)_6]$ and ferric ammonium citrate. It is then applied to a receptive surface such as paper. The fundamental chemistry in the cyanotype process begins with the exposure of ferric ammonium citrate to UV light, which causes the photoreduction of Fe(III) to Fe(II) and the citrate is oxidized to acetone dicarboxylic acid according to the following reaction:[15−18]

$$2Fe^{3+} + C(OH)COOH(CH_2COOH)_2 \rightarrow 2Fe^{2+} + CO(CH_2COOH)_2 + CO_2 + 2H^+$$

The blue print is revealed resulting from the formation of the Prussian blue $Fe^{III}{}_4[Fe^{II}(CN)_6]_3 \cdot nH_2O$ (n = 14−17) according to the following mechanism:

$$Fe^{2+} + [Fe^{III}(CN)_6]^{3-} \rightarrow Fe^{3+} + [Fe^{II}(CN)_6]^{4-}$$

$$4Fe^{3+} + 3[Fe^{II}(CN)_6]^{4-} + nH_2O \rightarrow Fe^{III}{}_4[Fe^{II}(CN)_6]_3 \cdot nH_2O$$

After sufficient exposure, the paper is washed in a tray with running tap water for about 5 min to remove the soluble unexposed salts. We obtain here a good blue permanent image, as Prussian blue is practically insoluble in water.

We first started this work by directly preparing Prussian blue from potassium ferricyanide $K_3[Fe(CN)_6]$ and iron(III) chloride $FeCl_3$ according to the following mechanism:

$$3[Fe(II)(CN)_6]^{4-} + 4Fe(III) + nH_2O \rightarrow \{Fe(III)_4[Fe(II)(CN)_6]_3\} \cdot nH_2O$$

Second, different electrochemical cells were studied to review oxidation−reduction theory. Finally, students were asked to explain the formation of the blue image from the potassium ferricyanide $K_3[Fe(CN)_6]$ and ferric ammonium citrate by using sunlight or UV radiation.

During the process, students became familiar with some laboratories activities. Indeed, students realized the relationship between the nature of the radiation (sunlight or UV radiation) and the colors of their photograph. Moreover, some students put into evidence the influence of the time of radiation on the quality of their photograph. Some students quickly assimilated the mechanism taking place during the formation of Prussian blue. Others had to work really hard to develop thorough understanding. We would like to insist on the fact that this experimental approach of oxidation−reduction theory is a really nice way to teach. Indeed, the influence of each parameter is very quickly visible. Therefore, one can make different attempts to try and understand in details the role of light and the chemical mechanism at stake in the formation of the photography. Students spent around 5 h in the laboratory, multiplying experiments and questions. And they were then proud to exhibit their different attempts in the halls of the University. And we firmly felt that by presenting them precise and demanding chemistry contents motivated by an artistic activity we could obtain much greater attention and efforts from them than what we are used to in more classic and formal courses.

■ HAZARDS

Photography experiment can produce toxic gas by contact with acid. Indeed, in addition to the potassium ferricyanide, cyanide gas is released. Therefore, it is important to work in absence of acid in the laboratory during the photography session.

■ CONCLUSION

Our lab-oriented and "humanistic" introduction to chemistry was successful. Our students took more interest in chemistry than students following a standard introduction to our discipline. Due to the practicability of this experiment, we are convinced that the laboratory will be a unique learning environment. Practical work will be used here to engage students in investigating, discovering, making inquiries and problem-solving activities as practiced in the case of the Egyptian blue synthesis. As a result of this approach, we are convinced that students will retain the ability of asking more reflective questions even when new principles of chemistry are presented in a purely theoretical and nonexperimental way, and therefore develop high-level learning skills.

In our opinion, it is worth to follow this direction even if it costs more work and if it shakes the teachers' habits. In any case, we go on with this extension of Mahaffy's idea during the second year of our bachelor program where student are introduced to crystallography.

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Notes

The authors declare no competing financial interest.

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