Educación Química

Crystallography case studies at the undergraduate level

Peter Josue Rosado Flores[1]

Abstract

Powder diffraction is not a characterization method alien when it concerns inorganic chemistry and material science. At the undergraduate level, however, it is rare to come upon the teaching of these methods (probably due to the lack of expensive instrumentation that could ascend the $500,000 USD mark), and instructors mostly focus on the theory. This work provides techniques to construct these case studies that could be utilized in a classroom environment, particularly at the intermediate and advance inorganic chemistry level. Therefore, the purpose of this study seeks to contribute implemented ideas to the facilitation of crystallography education at the undergraduate level using the case study method.

Keywords

Powder diffraction, crystallography, chemical education, inorganic chemistry, case studies, X-ray diffraction

Casos de Estudio de Cristalografía a Nivel Subgraduado

Resumen

La difracción de polvo no es un método de caracterización ajeno en cuanto a la química inorgánica moderna y la química de materiales consta. A nivel pre-grado, sin embargo, es raro observar la enseñanza de estos métodos (muy probable dado a la falta de instrumentación, que puede ascender en costo a los $500,000 dólares estadounidenses), y simplemente los instructores se enfocan en teoría. Este trabajo provee técnicas para construir casos de estudio que pueden utilizarse en el salón de clase, particularmente en el salón de química inorgánica intermedia e avanzada. El objetivo de esta didáctica es discutir ejemplos de casos de estudio referentes a la educación en cristalografía utilizando simuladores accesibles y expandir mas esta creciente rama de la química.

Palabras clave

Difracción de polvo, cristalografía, educación en química, química inorgánica, casos de estudio

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Introduction

A previous report detailed the use of available crystallography software at the undergraduate level at Georgia College (Rosado Flores, 2018). It is important to recognize that fundamentals of inorganic chemistry form an essential part of studies that occur after undergraduate degrees are conferred (particularly at the doctoral level). If the student decides to study synthetic inorganic chemistry, for example, at some moment he will encounter the topic of crystallography. Therefore it is important to plant the seeds of knowledge of such topics *before* undergoing such advanced studies. In the past there have been publications that have touched upon the topic of implementing crystallography at the undergraduate level, however, a large portion of these state the need for advanced instrumentation (Campbell, Powers, & Zheng, 2016; Malbrecht, Campbell, Chen, & Zheng, 2016; Grundwell, Phan, & Kantardjleff, 1999) and most 4 year colleges do not possess the funding to obtain such instruments.

The case study technique comes in handy in these cases, and it is a very popular technique in all areas of education (Bonney, 2015; Hemlin, 1996). It is a versatile technique which allows the student to apply their higher order abilities to a probable scenario. For example, case studied involving the mining industry can be developed, as X-ray diffraction (single crystal and powder) is used heavily in the identification of mineral clay bodies. In this way, companies can ensure efficient purity and extraction methods on their mining operations (Villiers & Verryn, 2007). Clays themselves possess a myriad of uses ranging from the confection of ceramics to functional materials (Brindley, 1952; Dorofeev, Streletskii, Povstugar, & Elsukov, 2012). These are topics on items that are present in our daily lives but their origins and properties are rarely discussed inside the classroom, outside of specialized courses. It is evident that if students are exposed early on to real life, modern situations, they will develop vital critical thinking skills (Unsar & Engin, 2013; Frerichs, 2013).

Crystallography Resources

With the advent of the World Wide Web has come the ease of sharing of data between scientists and science enthusiasts. There are accessible materials for instructors who wish to implement (or create) their own case studies. For the case studies specific to this article, the program CrystalDiffract® was utilized, published by the company CrystalMaker© (Crystal Maker Software, 2019). This software suite acts as a "Powder X-ray diffraction" simulator* and is available to students if a departmental license is purchased. This program was utilized using a personal license to design the mixtures described in this article, and all licensing policies were observed. If no funds are available to purchase specific software, there are free databases online that the instructor can access such as the "Crystallography Open Database" (Crystallography Open Database, 2019) and the "Crystal Morphology Database". The latter is published by Portland State University in Portland, Oregon (Crystal Morphology Database, 2019). Lastly, Mercury Crystallography is a popular "freeware" software published by the Cambridge Crystallographic Data Centre (Cambridge Crystallographic Data Centre, 2019). Powder diffraction data can be obtained from published .cif files and converted in CrystalDiffract® and Mercury. Some powder patterns in this study (those in Example # 2) were obtained from the database and imported into the programs. Though Mercury does not allow for the analysis of multiple patterns at one time, patterns can be printed and manually overlaid in transparent paper to convey the essentials of the studies (students particularly enjoy this since it allows them to treat the studies as puzzles).

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Specific methods

The class size where these case studies were implemented varies each year. Typically, class size ranges from 10 – 20 upper level students who have taken intermediate inorganic chemistry (for those enrolled in advanced inorganic chemistry) or are enrolled in it (for those enrolled in inorganic chemistry laboratory). Students are generally chemistry majors; thus, they have a focused background in chemistry.

Ideas

To prepare case studies the instructor requires three things: experience in the field, imagination, and a sense of reality (e.g. does the study make sense?). Data from recent real events related to the topics can be harvested for ideas, keeping in mind the relevance of the topics. Using information from real events fosters discussion and critical thinking amongst students. This promotes active learning, in which students seek out their own answers instead of always looking towards the instructor. The instructor then becomes a guide instead of a major source of information.

Activities (Case Study Examples)

Several case studies were designed. Both case studies contain distinct scenarios where students need to implement the scientific method and their knowledge of X-rays to complete the assignments. In Example # 1 (Figure 1) the discovery of a new type of clay in the northern mountains of Puerto Rico is discussed. The student must first think "outside of the box" and look for information of geography and geology of this area (an area called the Northern Karse) to complete the work. In Example # 2 (Figure 2-4), the student assumes the identity of a quality control analyst for a fictitious cement company called *Taíno Cements*, here the student needs to identify the missing phases of a cement mixture and compare to a standard. None of these examples require expensive instrumentation, other than the software described (if obtained). The two examples are discussed below.

Example # 1

"A new type of clay in Puerto Rico"

Narrative:

"A geologist, Dr. Price, assigns you a clay sample harvested from the northern coast of Puerto Rico, an area called the Northern Karst. It is an arid area that forms part of the Central Mountain Range. This area is very rich in calcite, $CaCO_3$, and dolomite, $CaMg(CO_3)_2$. Dr. Price is not knowledgeable in Powder X-ray diffraction and asks you to analyze the sample for him to determine the composition of the new clay. The geologist has provided you with a sample and preliminary powder patterns."

Instructions:

Each group will have an unknown sample. Each sample contains different components. Your assignment is to answer the questions below and identify the clay unknown with the provided patterns. You will have to report the identity of your clay sample to the instructor.

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Note: It is recommended that you work in groups, but each member has to have their own answers and conclusions. Additional Note: Remember that you will not be able to "quantify" your sample components by merely looking at the powder pattern. Intensities in patterns are not proportional to the amount of sample, but to the orientations of components in the sample. The patterns do not provide information on the quantities of components. To obtain this information, further processing is needed. In addition, simulations do not take into account any artifacts that come up in experimental patterns.

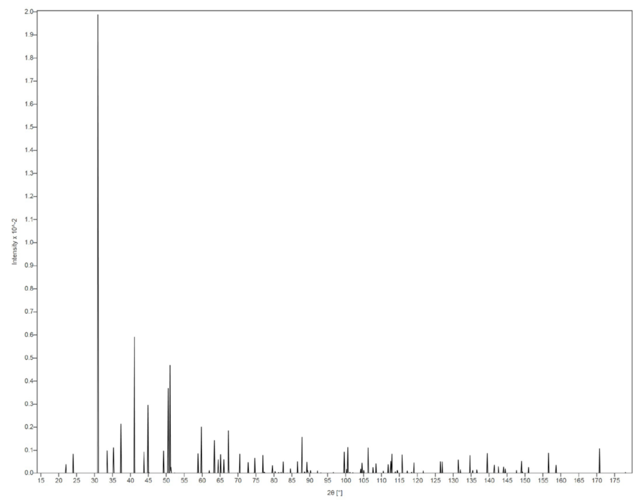

Figure 1. Simulated powder pattern of dolomite. This can be one of the individual patterns provided to students.

Example # 2

"Trouble at *Taíno Cement Company*"

Narrative:

"You are an analyst for the *Taíno Cement Company*. Your work consists in analyzing the quality of cement samples as they come out of the production plant. One morning, your boss- the quality control manager, calls you to let you know that the previous' night cement lot was produced a bit discolored and powdery. In addition, the manager tried to prepare some concrete with the cement and obtained a very brittle material. The manager has asked you to design an experiment that involves multiple analytical techniques, including Powder X-ray diffraction, to determine the components of the cement and their purity. Likewise, the manager has provided you with a pattern of the standard of how cement should look like to compare. With your experience with cement samples, you know that cement is a mixture of various components. The final mixture of *Taíno Cement* should contain characteristics peaks of gypsum, calcite, dolomite, aluminum oxide, among others. The final product must possess a comparable composition to your standard pattern. Absence of some of these components may affect the properties of the resulting cement."

Instructions:

Each group will have powder patterns that reflect the cement sample mixture at different stages of production. Your task is to answer the questions and identify the phases of the mixture and compare to the standard. You will have to report your results to your supervisor

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in an ACS style report. *Note: It is recommended that you work in groups, but each member has to have their own answers and conclusions. Additional Note: Remember that you will not be able to "quantify" your sample components by merely looking at the powder pattern. Intensities in patterns are not proportional to the amount of sample, but to the orientations of components in the sample. The patterns do not provide information on the quantities of components. To obtain this information, further processing is needed. In addition, simulations do not take into account any artifacts that come up in experimental patterns.*

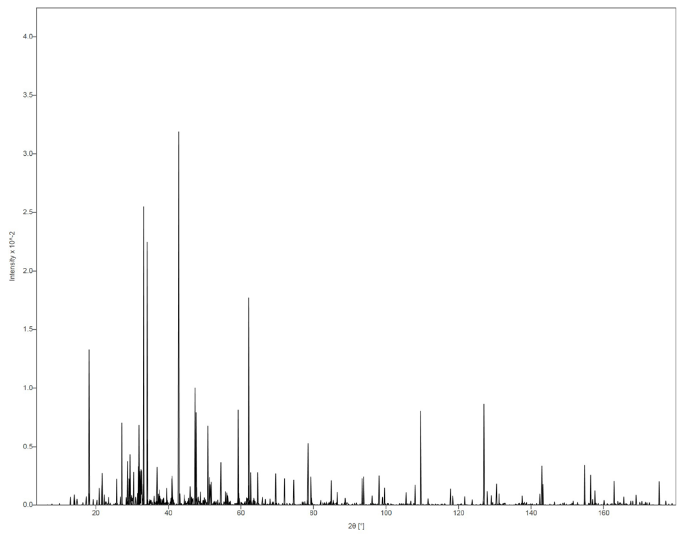

Figure 2. Pattern for a possible mixture of the final "contaminated" product (simulated). There are two components missing: gypsum and iron carbonate. Students need to find out which phase is missing or which phase does not belong to the standard sample.

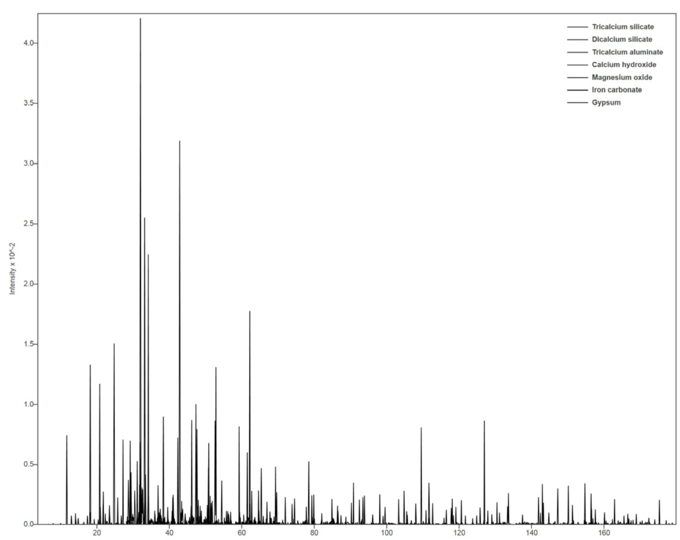

Figure 3. Example of a possible standard for *Taino Cement* (simulated)

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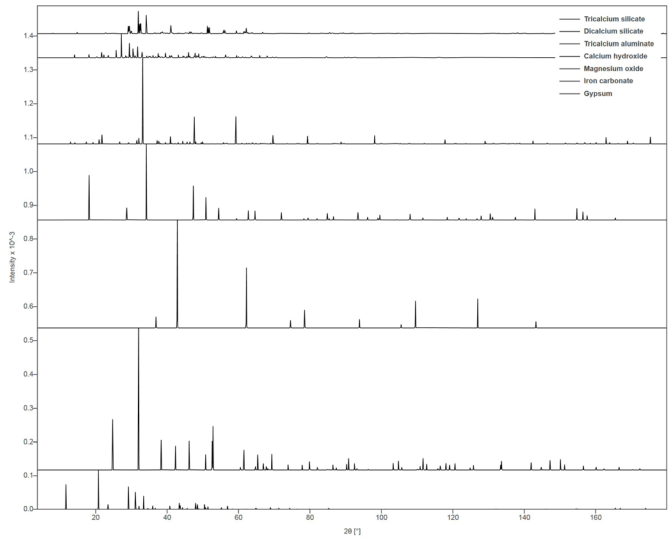

Figure 4. Example of a simulated standard with separated phases (overlay). The simulated, individual patterns, can be used as a method of identification of the unknown sample.

Questions to answer:

- What is powder diffraction?
- What does the Bragg equation tell you? Identify the pertinent variables and their relationships (equation 1).

$$n\lambda = 2d\sin\theta \qquad (1)$$

- What type of technique or process would you use to prepare the sample?
- What database would you access to verify that your hypothesis is true, regarding the identity of the sample?
- Provide at least 3 distinct methods of analysis from literature regarding the identification of clay mixtures. Provide a reference and a summary of each.
- Do your results agree with typical clay compositions for the Northern Karse area of Puerto Rico?
- Identify the components of your impure cement mixture. Compare to the standard.
- What components in cement would you need to look out for in your pattern to assure the sample quality?
- Provide at least 3 distinct methods of analysis from literature regarding the identification of cements. Provide a reference and a summary of each.
- Write an ACS Style report and submit to your instructor (Coghill and Garson, 2006)

Evaluation

Students involved in case studies were evaluated not only on the certainty of their answers, but also their critical thinking skills using, as an example, the rubric below (Table 1). By utilizing an established rubric, students could not only see where they went wrong, but could also reflect on such. The case studies described here have been implemented in Inorganic Chemistry Laboratory and Advanced Inorganic Chemistry for the past 3

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years. The class size ranged from 10-20 students. Qualitatively, students enjoyed the open discussion and felt a "sense of responsibility" when presented with the case studies. That is, from the author's perspective, they felt confronted with a real issue that needed a solution. As for quantitative data, 90% of students successfully identified the unknowns under a 3 hr. lab period. In addition, 70% of students scored above an 80 (B average) on the writing/reporting part of the assignment.

Table 1. An example evaluation rubric which is openly modifiable

	Score			
Evaluation Criteria	**Excellent 100%**	**Advanced 75%**	**Acceptable 50%**	**Unsatisfactory 0%**
Confidence	Data is presented in a confident manner from part of the analyst (student). It is also well supported by peer-reviewed literature (minimum 5). The report (and questions) also provide ample justification of the data.	There exists evidence of understanding and clarity, but it is not supported by primary literature (3 peer reviewed sources). The data is lacking representation.	There is no clarity nor presentation of the work. It is supported by less than 3 primary references.	No references nor analysis is present.
Analytical Skills	In the results and discussion section of the report, there exists a systematic analysis of the data (for example, when talking about the Bragg equation- calculation examples are provided). The data proves the identification of unknown or phases with certainty.	There exists an attempt at systematic analysis, but it is not clear. Does not provide examples of calculations or supporting theories. Provides the identity of the unknown, yet it is not certain.	N/A	There is no systematic analysis. Does not provide example calculations nor the identity of the unknown.
Information Skills	100% of the references are modern and respected (e.g. peer reviewed).	Only 50% of the references are modern and respected.	Only 25% of the references are modern and respected.	There are no references present. If there are references, none of them are modern and respected.
Communication Skills	The report is well written with no jarring grammatical errors. It also follows ACS (American Chemical Society) guidelines.	There are 4 grammatical errors that are jarring (they alter the meaning of results). Some sections of the report follow the ACS format.	There are more than 4 grammatical errors that greatly affect the meaning of the results. Only 25% of the report follows the ACS format.	There is no logical narrative to the report (no flow). The report seems hastily written, with many a grammatical error. It does not follow the ACS format.

Conclusions

Various case studies on Powder X-ray diffraction were designed that can be implemented in a chemistry classroom, particularly inorganic chemistry, advanced inorganic chemistry, solid state chemistry, and instrumental analysis. Two of these are discussed in this article. At Georgia College, the case study technique has been implemented in many courses in the efforts of introducing high impact, active learning practices into the curriculum. For the first time at GC, X-ray crystallography has been implemented into the inorganic chemistry curriculum. Students' abilities were challenged and assessed via the rubric included in this work, where most could successfully identify the unknowns and answer the questions given. Crystallography education is a growing field where it is often hindered by expensive instrumentation and lack of focused expertise on the matter. More publications where faculty can utilize methods such as the case study method will definitely expand the field and make it more accessible to those interested.

Conflict of interest

The author of this work declares no conflicts of interest.

Acknowledgements

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Campbell, M. G..; Powers, T. M.; Zheng, S-L (2016). Teaching with the Case Study Method to Promote Active Learning in a Small Molecule Crystallography Course for Chemistry Students. *Journal of Chemical Education*. *93*(2). 270-274

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Crystallography Open Database, consultada Octubre 15, 2019, en la URL http://www.crystallography.net/cod/

Dorofeev, G. A.; Streletskii, A. N.; Povstugar, I.; Elsukov, E. P. (2012). Determination of nanoparticle sizes by X-ray diffraction. *Colloid Journal*. *74*(6) 678-688

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Supplementary information

Additional literature used in the activities is presented below. Instructors and students alike are welcome to add to this list.

Case Study I

"A new type of clay in Puerto Rico"

Important references for instructor:

Jeffries, C. D., Bonnet, J. A., & Abruña, F. (1). The constituent minerals of some soils of Puerto Rico. *The Journal of Agriculture of the University of Puerto Rico*, *37*(2), 114-139. Retrieved from https://revistas.upr.edu/index.php/jaupr/article/view/12756

The reference above is important for students to understand soil compositions in the Puerto Rican geographic landscape. This can be provided for students or "hinted" at during the discussions.

Acevedo, G., Kunze, G. W., & Lugo-López, M. A. (1). Morphological, Mineralogical, and Physico-Chemical Characteristics of Some Dark Clay Soils of Puerto Rico. *The Journal of Agriculture of the University of Puerto Rico*, *60*(4), 491-507. Retrieved from https://revistas.upr.edu/index.php/jaupr/article/view/10494

The reference above is also important for students to understand soil compositions in the Puerto Rican geographic landscape, particularly the included X-ray diffraction measurements can guide students into understanding further the theory behind X-ray diffraction *and* how some clays should look. If the instructor wished to include thermal analysis data as additional information for the activity, this is also readily available in the article.

Munoz, M. A., Lugo, W. I., Santiago, C., Matos, M., Rios, S., & Lugo J. Taxonomic Classification of the Soils of Puerto Rico, 2017, *Bulletin 3*. Retrieved from https://www.uprm.edu/tamuk/wp-content/uploads/sites/299/2019/06/Taxonomic_classification_soils_PR_2018_reduced.pdf

The above is a recent bulletin from the University of Puerto Rico that provides the verbiage of the field necessary for students and instructors to understand the first case study. Students are encouraged to use this verbiage of the field when preparing their activity reports.

Case Study II

"Trouble at Taino Cement Company"

Important references for instructor:

Dunuweera, S. P., Rajapakse R. M. G., Cement Types, Composition, Uses and Advantages of Nanocement, Environmental Impact on Cement Production, and Possible Solutions. *Advances in Materials Science and Engineering*, 2018, 1-11.

A recent review on cement types. The article is currently open access and available. Students and instructor may access this for some background material before engaging in the activity.

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Olanitori, M. L., Causes of structural failures of a building: Case study of a building at Oba-lle, Akure. *Journal of Building Appraisal* (2011), 6, 277-284.

A 2011 case study of a building in Oba-lle, Akure, Ondo State Nigeria. The effects on the quality of materials used to produce and mix the concrete are explained- which resulted in failures of a two-story building in the location. While the article does not provide a background in X-ray diffraction, it does provide a real-life causation of what can happen if concrete is not produced to standard. Many more similar cases are available in the primary literature.

Jadhav, R., Debnath, N. C., Computation of X-ray powder diffractograms of cement components and its application to phase analysis and hydration performance of OPC cement. *Bull. Mater. Sci.* (2011), 5, 1137-1150.

The above is an article which references computer X-ray powder diffractograms. Some component signals may be found here and compared to those produced by CrystalDiffract.

Additional Note: No student responses are recorded since they will vary on the simulation provided by the instructor. Thus, a result like this would vary on an instructor to instructor and student to student basis. However, the author found that students generally are able to generate the pertinent literature required to answer the case study questions. The advantage of case studies lies on the fact that they are highly adaptable to the student learning needs.

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