INTRODUCING ARCHAEOMETRY ON A HIGH-SCHOOL EXCELLENCE PROGRAM: ENGAGING STUDENTS TO MATERIALS SCIENCE AND CULTURAL HERITAGE SUBJECTS

Suset Barroso-Solares[1], A. Carmelo Prieto[1], Javier Pinto[1]

[1] Archaeological and Historical Materials (AHMAT) Research Group, Condensed Matter Physics, Crystallography, and Mineralogy Department, Faculty of Science, University of Valladolid, 47011 Valladolid (SPAIN)

Abstract

The Castile y Leon region (Spain) offers a two-year high-school excellence program for highly motivated students, in which the University of Valladolid (Spain) is involved. During the first year, the students visit the University of Valladolid's research facilities, as well as attend specialized talks on the areas of knowledge of their interest. Then, in the second year, they have the opportunity to develop a scientific project under the supervision of one High School and one university professor. These projects are intended to provide a unique first contact with actual research activities for these students, being usually focused on specific research fields.

The Archaeological and Historical Materials (AHMAT) Research Group of the University of Valladolid has recently developed a new scientific project for this high-school excellence program, entitled “Studying ancient history and cultural heritage throughout materials science”. This is the first project introducing the archaeometry field of study on this high-school excellence program and, as correspond to this subject, provides multidisciplinary training to these young students.

In this project, the students learn how to use and provide a basic interpretation of the results of useful experimental techniques on Archaeometry such as Raman and infrared spectroscopies, optical microscopy, and X-ray diffraction. Also, they learn about the evolution of construction materials throughout History, the diverse natural pigments employed by some of the greatest painters of all times, the preservation of our monuments, and the lessons that the archaeological findings could provide about the past of their region. In all the cases, the basic concepts are reinforced by allowing the students to reach their own answers about proposed case studies by performing experimental analysis of a selection of cultural heritage samples.

Herein, the design and development of this scientific project for the high-school excellence program are described, with a particular emphasis on identifying the teaching opportunities of materials science concepts, the promotion of cultural heritage awareness and the development of scientific vocations. Finally, the efficiency and success of this project are evaluated, taking this feedback about its implementation into account to propose further improvements.

Keywords: spectroscopy, pigments, ancient glass, mortars

1 INTRODUCTION

Cultivate scientific vocations by allowing high-school students to interact with research teams at the University is one of the main objectives of the High School Excellence/Research two-year program of the Junta of Castile and Leon (Spain).[1], [2] The first year is dedicated to briefly introduce High-School students to diverse specialized research/knowledge fields by attending several talks provided by professors of the University of Valladolid (Spain). Moreover, several top research laboratories are visited along with the program, providing a detailed view of the scientific activity at the University.

These first contacts with diverse research fields at the University are just the initial step of the program. In the second year, these High-School students with top qualifications select a research project of their interest, among a broad topics’ selection offered by the professors at the University of Valladolid. Then, they will dedicate about 35-40 hours to complete the research project, working at the University facilities under the supervision of experienced researchers.[1], [2]

An implicit responsibility lies in the selection of topics proposed to the students. Highly specialized and focused topics could provide a biased perspective of the research activity, risking slowing down instead of cultivating scientific vocations. Accordingly, research topics involving multidisciplinary approaches and a diversity of experimental/theoretical techniques are particularly welcome.

With this aim, the "Archaeological and Historical Materials" (AHMAT) Research Group of the University of Valladolid proposed a new research project on the Archaeometry field for the course 2020-2021, entitled "Studying ancient history and cultural heritage throughout materials science". As stated by Liritzis et al., "*Archaeometry is Science at the Service of Human History and Art*",[3] providing unique opportunities to develop multidisciplinary training programmes. In particular, the approach followed by the AHMAT Research Group involves the use of diverse techniques of the materials science field for the study of the past of the Duero basin, the construction and preservation of cultural heritage, the technologies and materials employed in ancient glass, and the preferred pigments of some of the greatest painters of History. Therefore, the students enrolled in this program will receive not only basic training on materials science but also learn about the cultural heritage and history of their region, their country, and the Mediterranean.

Herein, the contents, structure, and methodology of this research project are summarized. In addition, practical advice on its implementation and potential improvements, following the student's feedback, are included.

2 METHODOLOGY

This project for the High School Excellence/Research program was organized into diverse tasks, which are described in Table 1. The tasks and activities were designed and scheduled aiming to follow an appropriate learning curve. In the first tasks, the main concepts about the Archaeometry field and the experimental techniques to be employed were provided. Then, specific case studies were proposed, providing a historical background for each of them. Each case study involved diverse materials and experimental techniques, and the objective of the study was established from the beginning (i.e., the historical question to answer). This is an important issue, as this project aims to teach the student that even the most detailed and advanced physic-chemical characterization of cultural heritage materials lacks sense without a historical context. Finally, the student should prepare a written report, as well as an oral presentation, showing the obtained results and, most importantly, the learning process followed.

Table 1. Activity distribution.

Tasks	Specific activity	Details	Experimental techniques	Conclusions
1	Presentation	Initial contact between the High-School students and the University professors	-	Learn about the motivation of the students and their areas of interest. Introduce the student to the research facilities and workspace
2		Laboratory tour	-	
3	Theoretical and historical concepts	Archaeometry introductory lesson	-	The aim, approaches, and examples of the Archaeometry field are briefly presented to the students. The samples to be studied along the project are introduced, providing a historical context, and highlighting the relevance of the experimental results achievable. Description of the fundamentals of the experimental techniques to be employed during the project
4		Context of the samples to be studied	-	
5		Basis of the experimental techniques	Raman and Fourier Transform Infrared (FTIR) spectroscopy, X-ray diffraction	

6	Construction materials along History	Study the composition of historical mortars	FTIR spectroscopy, X-ray diffraction	Understand the architectural evolution and the selection of the materials on the construction of the Castle of Coca (Coca, Segovia, Spain)
7	Cultural Heritage preservation risks	Study degradation/alteration processes	Raman spectroscopy	Identify the composition of efflorescence on the surface of altered petrous samples
8	Velazquez's palette: analysis of historical pigments	Study of historical pigments	Raman spectroscopy	Create a small Raman spectra database of historical pigments and use it to identify pigments employed by Velazquez in his masterpieces
9	Our ancestors, the Vaccaei	Study of ancient glass beads	Raman spectroscopy	Understand the technological development involved in the fabrication of the glass beads. Learn about the ways of life, funerary rituals, and commercial relationships of the Vaccaei
10	Presentation and discussion of the final work	Written report and Oral presentation		Introduce the basic skills to write scientific reports, public speaking, and science outreach

3 RESULTS

A summary of the activities developed in each task is presented in this section, detailing the practical activities carried out by the students.

3.1 Tasks 1 and 2: Presentation

In the first contact with the High School students is essential to understand the motivations of the students. Knowing what aspects of the project proposal impelled the students to choose it would allow developing a successful project. Then, the students visit the research facilities in which the project will be developed, getting acquainted with the workspace and learning about safety considerations and good practices to work in the laboratory.

3.2 Tasks 3, 4, and 5: Theoretical and Historical concepts

As a multidisciplinary field, a proper introduction to an Archaeometry project requires considering and learn diverse aspects. First, the Archaeometry field is introduced, pointing out that successful and valuable research on this field requires a synergy between the analytical techniques employed and the historical interpretation (i.e., focused on the kind of samples proposed in this project, the materials scientists and the archaeologist/conservators should work together).

Then, the samples to be studied are introduced, providing historical background of each of them.

3.2.1 Mortars from the Castle of Coca (Coca, Segovia, Spain)

The Castle of Coca (Coca, Segovia, Spain) is one of the summits of the Gothic-Mudejar architecture on the Iberian Peninsula,[4] being classified as a National Historic Landmark. Among other features, the castle present magnificent geometric decorations composed of brick and mortar lines. The AHMAT Research Group had the opportunity in 2020 of studying the composition of the mortars from different areas of the castle, being one of the first analytical studies of this monument. Four mortar samples from this study, presenting clear differences in their composition or even remaining pigments (Figure 1), were selected for this project to be studied by FTIR spectroscopy and X-ray diffraction.

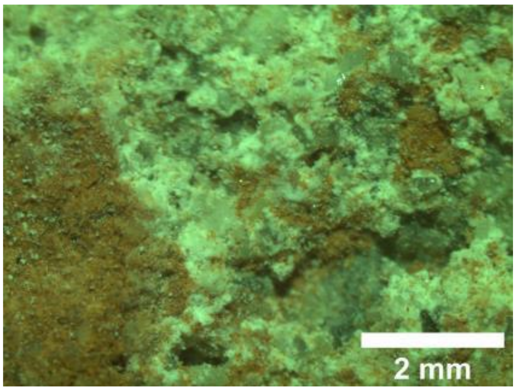

Figure 1. Micrograph of one of the mortar samples showing remaining of a red pigment.

3.2.2 Petrous substrates with the presence of salts

One of the main risks for the preservation of cultural heritage buildings and monuments is salt weathering, which is an alteration procedure expected to increase with climate change.[5] Samples of petrous substrates affected by the presence of salts were selected in order to study the presence and composition of the salts by Raman spectroscopy (some of them identifiable as efflorescence (Figure 2)).

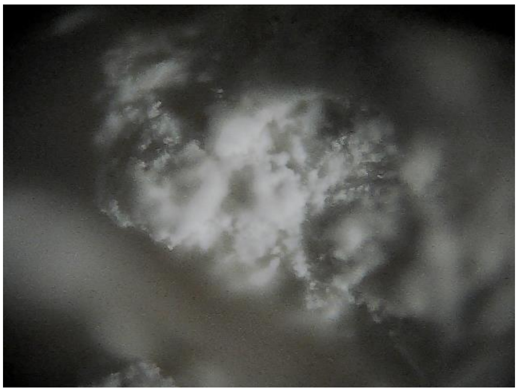

Figure 2. Micrograph of efflorescence on a petrous substrate.

3.2.3 Historical pigments

The history of the use of pigments started about 40.000 years ago, with cave paintings. Then, humanity has been identifying or developing new pigments throughout its history. As a consequence, some pigments are particularly related to some periods of our history, or have been available exclusively from a well-defined date, allowing us to identify false paintings.[6] A selection of pigments widely employed by Diego Velazquez (i.e., lead carbonate, calcite, azurite, vermilion, carbon black, hematite, and goethite) were provided for their characterization by Raman spectroscopy aiming to create a small database. Moreover, Raman spectra of diverse regions of Velazquez's paintings, such as *Adoration of the Magi,* were provided for their identification using the developed database.[7]

3.2.4 Ancient glass beads

Glass pieces were sophisticated goods in the Protohistory of the Iberian Peninsula. The technological development required for their production suggests that their origin should be related to some of the dominant civilizations of the Mediterranean. The presence of a large number of glass beads (over one thousand) on the archaeological site of the necropolis of "Las Ruedas" (Padilla de Duero, Valladolid, Spain) reveals intense commercial relationships of the local culture, the Vaccaei, who inhabited the sedimentary plains of the Duero valley from IV to I century BC. A couple of blue glass beads found in the necropolis were selected to be studied by Raman spectroscopy. In addition, Raman spectra of glass beads altered by the cremation ritual were provided to deepen the understanding of these materials. As Raman spectroscopy allows identifying the features of the glass network, the student will learn about the glass manufacturing processes and technological development in ancient times.[8]

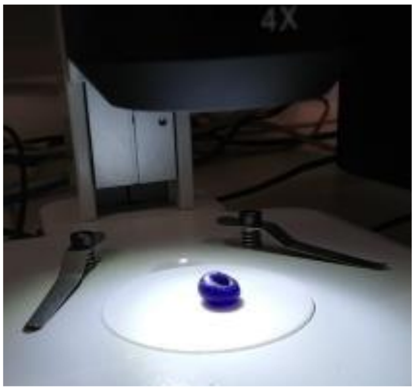

Figure 3. Ancient blue glass bead ready to be studied by optical microscopy.

Finally, the experimental techniques that will be used along the project are explained. The fundamentals of the Raman and FTIR spectroscopy, adapted to High-School level, are presented in detail. Also, the measurement procedure using both techniques is described, as they will be later employed by the students. Moreover, a simplified description of the X-ray Diffraction technique is provided, as the student will be provided with X-ray Diffractograms in one of the Tasks of the project.

3.3 Task 6: Construction Materials Along with History

The first contact of the student with the experimental work happens by studying mortars using FTIR spectroscopy. The use of is technique, from an experimental point of view, is quite simple, providing the students with confidence about their skills to operate in an actual research laboratory.

After obtaining the spectra, the students were provided with information about the IR absorption bands of the main elements commonly present in historical mortars (e.g., gypsum, calcium carbonate, feldspars, quartz). From this information, the students were capable of successfully identifying the main IR absorption bands in the obtained spectra. Then, a comparative study of the diverse samples analyzed allowed them realizing of the diverse relative contents of the calcium carbonate and feldspars and quartz phases, as well as of the presence or absence of gypsum.

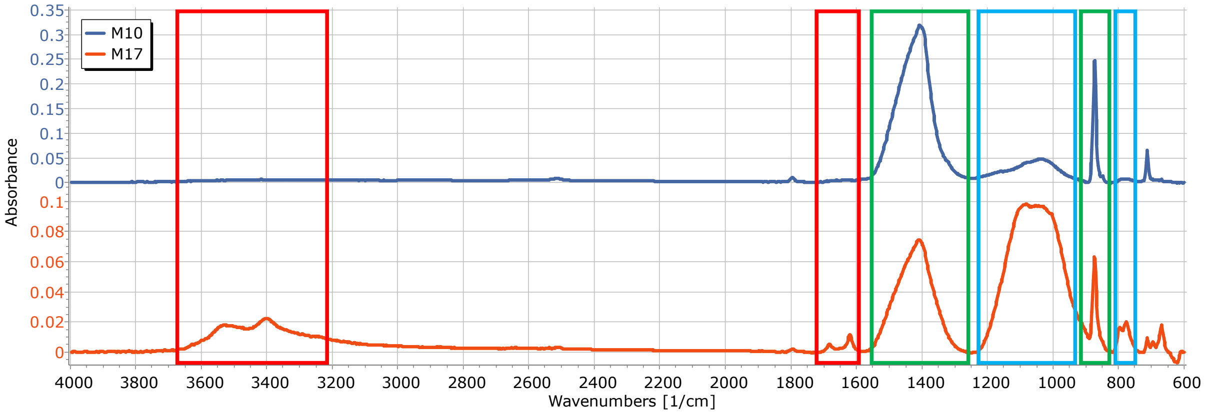

Figure 4. FTIR spectra of two representative mortar samples showing the characteristic features of gypsum (red), calcium carbonate (green), as well as feldspars and quartz (blue).

Moreover, once the potential composition of the studies mortars was identified by FTIR spectroscopy, the students were provided with X-ray diffractograms of the samples, including the identification of the diverse phase. They found that the mortars could present small amounts of a few additional phases, such as illite, which were not easy to identify on the FTIR spectra, and that the actual relative contents of the main phases are not necessarily related to the relative intensity of their IR absorption bands. Accordingly, the use of data from the two experimental techniques gave them perspective about the potential of each technique, as well as of the advisable complementary use of experimental techniques in the Archaeometry field.

3.4 Task 7: Cultural Heritage preservation risks

In the second experimental task, the students were introduced to the Raman spectroscopy technique. First, they learn how to use this technique by obtaining spectra of common minerals such as calcite, gypsum, quartz. Then, they were provided with the samples presenting salt damage with the task of identifying the composition of the petrous substrate and the salts.

Using the Raman spectroscopy in backscattering microscopic mode, the students identified non-altered regions of the samples and quickly realize that the obtained spectra correspond to those obtained with calcite during the previous training. Once the substrate was identified, they look for the presence of salts on the surface (Figure 2). They obtained spectra combining the features of the calcite with additional peaks, which they compared with the previously obtained spectra, finding that the new peaks correspond to gypsum. Then, it was explained to the students that, in the case of the studied samples, the gypsum provenance was a possible non-documented previous conservation intervention. This example showed the students how helpful can be this kind of analysis for the preservation of our cultural heritage.

3.5 Task 8: Velazquez's palette: analysis of historical pigments

In this task, it was discussed the potential use of a technique such as Raman spectroscopy directly on cultural heritage or art pieces. The students started by creating a small database of historical pigments, acquiring Raman spectra of a selection of historical pigments (Figure 5). During the acquisition of these spectra, the students realize that Raman spectroscopy handled without care could affect the studied materials. In particular, they found that both goethite and azurite could be easily degraded by laser irradiation, requiring very low irradiation power and very long acquisition times to achieve acceptable spectra of non-altered samples.

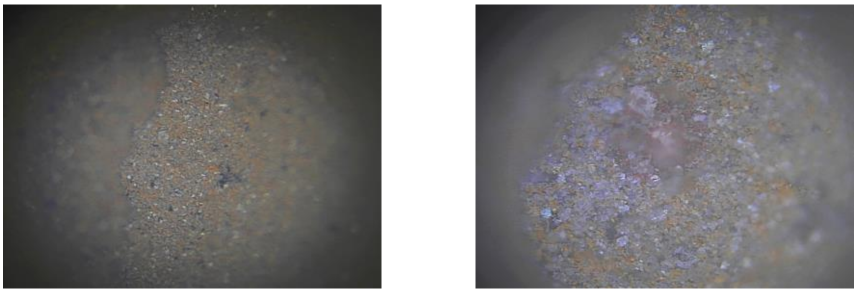

Figure 5. Micrography of the surface of a pigment before (left) and after (right) being altered by the laser irradiation, showing a noticeable alteration.

Once their database was ready (Figure 6), they were handled several actual Raman spectra of Velazquez's paintings, available in the literature.[7] By identifying the main peaks of the spectra of their database and comparing them with those of the provided Raman spectra of Velazquez's paintings, the students were able to ascertain that Velazquez employed those same pigments in his masterpieces. Moreover, they realize the expertise and carefulness required to perform this kind of study on actual cultural heritage samples.

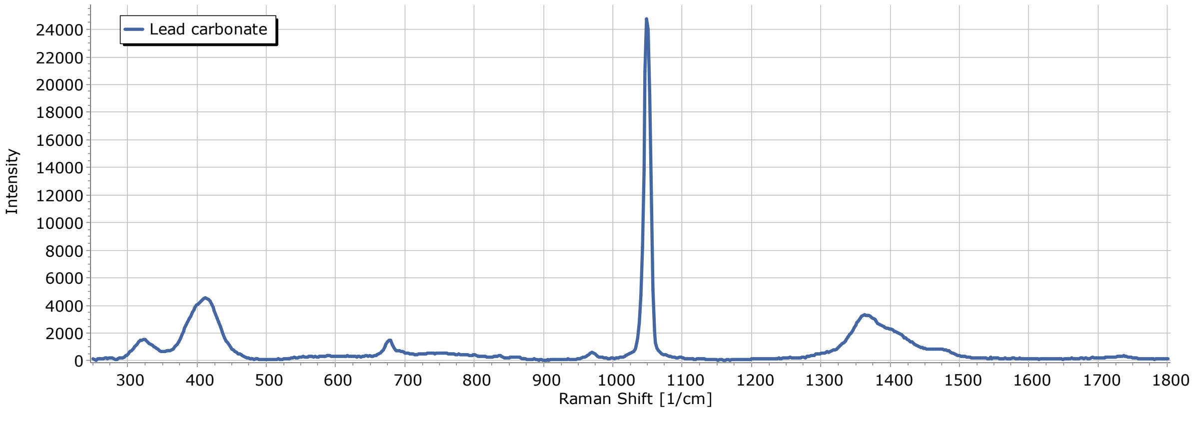

Figure 6. Raman spectra of a historical pigment based on lead carbonate obtained by the students.

3.6 Task 9: Our ancestors, the Vaccaei

In the last experimental task, the students deepen on the capabilities of Raman spectroscopy for the study of ancient materials. They study ancient glass beads. First, they obtained the Raman spectra of a couple of blue glass beads (IV-I BC). As the chromophore employed in these beads was mainly cobalt at trace levels, the identification of the pigment was not possible by Raman spectroscopy. However, the features of the glass network (i.e., the degree of polymerization of the silicon oxide tetrahedra) can be studied by Raman spectroscopy.[9] In addition to the spectra obtained experimentally, the students were provided with Raman spectra of additional samples affected by the cremation ritual.

To perform such analysis, it is necessary not only to identify the position of the main Raman peaks/bands but to perform a more advanced treatment and analysis of the obtained spectra. The students learn the basics of the spectra treatment (e.g., baseline subtraction) and how to perform the deconvolution of the spectra into the main Raman bands of glass using specialized software.

This analysis allowed obtaining the integrated intensities of the δ (Si-O) bending bands centred at around 500 cm^{-1} (A_{500}) and of the ν (Si-O) stretching bands centred at ~1000 cm^{-1} (A_{1000}). The ratio between both integrated values is known as the polymerization index ($I_p = A_{500}/A_{1000}$), and its value is related to the composition of the glass and its firing temperature, and therefore to the technological level of its manufacturers.[9] From the obtained data, the students correctly obtained I_p values about 1.0-1.1 for the well-preserved blue glass beads, which correspond to firing temperatures about 1100-1200 °C. On the contrary, the provided spectra of the samples altered by the cremation ritual shown I_p values about 0.5, which corresponds to temperatures of about 600 °C.[8]

Then, on the one hand, the students determine that the cultures that manufacture these ancient glass beads were able to reach temperatures up to 1100-1200 °C in a furnace. On the other hand, they realize that the temperature of about 600 °C found in the altered glass beads corresponds to the temperature reached during the cremation ritual, which altered the glass network of the surface of the glass beads.

3.7 Task 10: Presentation and discussion of the final work

At the end of the project, the students should organize the obtained results and relate them with the theoretical concepts presented along with the project. They should highlight how the obtained results help in the understanding of History, technological development, or art. They should prepare a written report, as well as a presentation that they will expose to other students and professors.

3.8 Comments about the implementation of the project

The development of the project has been positively evaluated by the involved students and professors, as well as other University and High-School professors and students attending the final presentations. In fact, it has been encouraged to keep this project proposal for the next course. The involved students have pointed out that they have never heard before about this research field, but the proposal description was attractive, as they never expected to find such strong relationships or synergies between physics or chemistry and history, art, or archaeology. Accordingly, it can be stated that the project fulfils the objective to publicize this research field.

Some potential improvements were also pointed out after this first experience. On the one hand, for the next year it has been proposed to include on the training program a visit to one of the archaeological sites which remaining are studied in the project (e.g., the vaccaean necropolis of “Las Ruedas” (Padilla de Duero, Valladolid, Spain). This activity will strengthen the message of the necessary relationship between the diverse areas of knowledge involved in Archaeometry. Moreover, potential quick *in-situ* measurements with spectroscopic techniques could be carried out during the visit. On the other hand, it should be evaluated if the project could benefit from narrowing the list of samples or historical contexts, in order to provide the students more time to deepen the understanding of each topic. Particularly, due to time constraints on the final presentation, this year, only one of the topics (i.e., ancient glass beads) was explained in detail by the students.

4 CONCLUSIONS

An innovative training program and research project on the Archaeometry field has been successfully implemented on the High-School Excellence/Research program of the Junta of Castile and Leon (Spain). This program offers multidisciplinary training to young students, showing how apparently quite diverse knowledge fields such as materials science and history, art, or archaeology can work together to improve the understanding of the history of our civilization.

ACKNOWLEDGEMENTS

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